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Interagency Energy/Environment R&D Program Report

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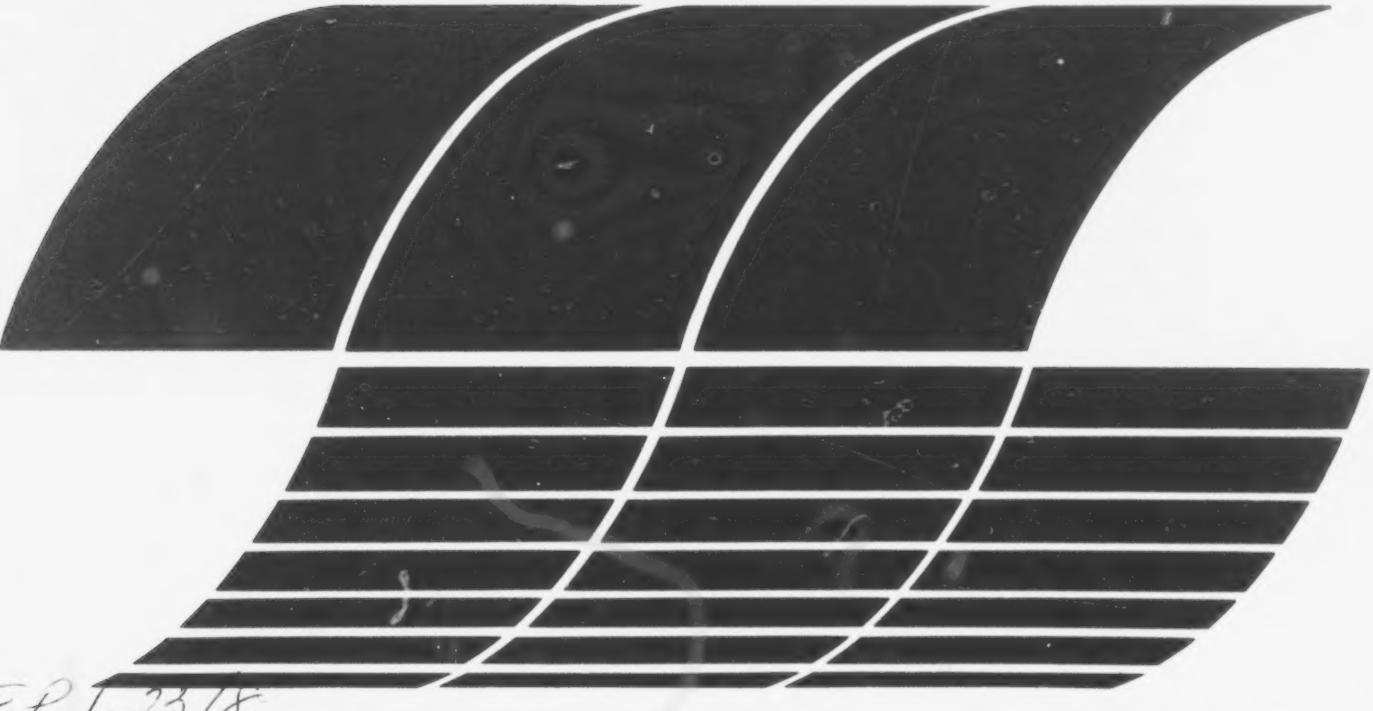

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EPA-600/7-80-117
August 1980

METHODOLOGY TO EVALUATE THE POTENTIAL FOR GROUND WATER CONTAMINATION FROM GEOTHERMAL FLUID RELEASES

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly efficient control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report develops a methodology and analytical techniques to evaluate potential impacts of geothermal fluid releases on the ground water environment. It is intended to assist both industry and regulators in planning geothermal developments through better prediction of environmental consequences.

Further information on the subjects of this report can be obtained from the Power Technology and Conservation Branch, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report provides analytical methods and graphical techniques to predict potential ground water contamination from geothermal energy development. Overflows and leaks from ponds, pipe leaks, well blowouts, leaks from well casings, and migration from injection zones can be handled by the methodology. General characteristics of geothermal systems and fluids and probable modes of release are included in the report to provide typical data.

The major steps of the procedure are to determine environmental concerns and release potential, to identify potential ground water contamination, and to evaluate significance of contamination. Analytical methods, data requirements, typical data and coefficient values are included.

The methodology may be used as a regulatory tool for predicting impacts or for testing control technologies. Geothermal developers can use the methodology to predict adverse impacts at development sites and select control methods for the conditions or locations where required.

This report was submitted in fulfillment of Contract No. 68-03-2671 by Tetra Tech, Inc. under the sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1

EXECUTIVE SUMMARY

PURPOSE OF PROJECT

The Environmental Protection Agency has contracted with Tetra Tech, Inc. to develop a methodology to predict potential ground water contamination resulting from geothermal energy development. Operational and accidental releases of geothermal fluid to ground water may be difficult to detect and corrective actions may not be practical. The presence of toxic constituents in some geothermal fluids emphasizes the need to prevent these fluids from reaching usable water supplies.

The objective of this project has been to develop a methodology for use by regulatory agencies and geothermal developers. The methodology developed is presented in this user's manual. Policy and procedural recommendations which minimize pollution hazards have been made. The development of the screening procedure included the characterization of geothermal fluids, the identification of potential release modes and locations, and the selection of appropriate analytical methods.

METHODOLOGY

The procedure consists of a set of analytical tools for predicting the fate of pollutants accidentally or intentionally released from liquid-dominated geothermal power plants. The major steps in the procedure are:

- Determine environmental concerns
- Determine release potentials
- Identify potential ground water contamination
- Evaluate significance of contamination

The two environmental concerns considered here are the contamination of usable aquifers by the geothermal fluid and mobilization of pollutants from the soil/rock matrix. Available chemical data for geothermal fluids were reviewed and compared to water quality standards for drinking water supplies, agricultural uses, and aquatic life. Twenty-three chemical species and total dissolved solids were identified as pollutants of concern. The chemical species include:

Aluminum
Ammonia
Arsenic[†]
Barium[†]
Boron
Cadmium[†]
Chloride[*]
Chromium[†]
Copper[*]
Fluoride[†]
Hydrogen Sulfide[*]
Iron[*]
Lead[†]
Lithium
Magnesium
Manganese[*]
Mercury[†]
Molybdenum
Nitrate[†]
Selenium[†]
Silver[†]
Sodium
Zinc[*]

[†] Included in primary drinking water standards (EPA, 1976a).
[*] Included in secondary drinking water standards (EPA, 1977).

Chemical compounds which may cause scaling problems, e.g., calcium carbonate, silica, and certain sulfates, were also considered. Geothermal fluid chemistries vary among sites and within a given reservoir. All of the chemical species listed above may not be present in significant concentrations at any particular site. Low pH geothermal fluids may mobilize heavy metals present in the soil/rock matrix.

Potential release locations and modes were identified from power plant design schematics. Diagrams have been prepared which show the types of releases which may occur at different points in the power plant and the conditions which increase the likelihood of a release. Geothermal experience to date indicates that pipe leaks occur most frequently, followed by well blowouts, valve jams, surface pond overflows, and well casing leaks. Information on corrosion rates of pipes carrying geothermal fluids under different conditions was compiled to enable the user of the procedure to identify piping subject to high corrosion rates. Methods are included to predict chemical changes (e.g., precipitation) in the geothermal fluid as it moves from the production well through the plant to disposal ponds or injection wells.

Analytical methods were selected to predict movement of pollutants from surface spills, from production or injection wells directly into usable aquifers, or from releases above or below usable aquifers. The transport equations include advection, dispersion, and reaction. Attenuation of pollutants by dilution, adsorption (or ion-exchange) and decay can be considered. A conservative evaluation can be made first by not considering adsorption and/or decay. If the calculations predict pollutant concentrations in excess of standards, the case with adsorption and decay should then be evaluated. Four analytical solution techniques were selected for use in the methodology:

- GEOHY-GEOQAL analytical method
- Advection-dispersion method
- Bernoulli-Darcy approach
- Mass-balance approach

The analytical method used for a specific release depends on the location and duration of the release. These analytical solution techniques were selected to minimize data requirements and calculations so that the methodology can be used in the early stages of geothermal development.

The significance of a potential release is evaluated by comparing the concentrations predicted at the plant boundary with the appropriate water quality standards. A release is considered significant if the resulting concentrations exceed any of the applicable use standards for the aquifer(s) in question.

The methodology provides a step-by-step procedure for predicting the potential movement of pollutants to ground water. Data requirements, example cases, constants, and representative data are included in the manual. The general data should be replaced by site-specific data whenever the latter are available.

RECOMMENDATIONS

In the course of this project several ways were identified to minimize the probability and effects of releases. The recommendations pertaining to surface spills are as follows:

- Use corrosion-resistant upgraded materials for critical plant components (e.g., piping and valves).
- Use pH control and/or additives to prevent scale buildup and corrosion.
- Use lined ponds for emergency storage of surface spills if underlying aquifers are usable.
- These ponds should be at least large enough to hold the precipitation from one-in-ten-year storm and four hours of total flow.

Recommendations for minimizing blowouts and subsurface releases are the following:

- Monitor the pressure of the production and injection wells continuously.
- Use carefully selected blowout preventers.

- Set injection pressures high enough to move fluid into injection zone but low enough to avoid fracturing of the formation.

Current research programs are investigating corrosion control methods for piping systems exposed to geothermal fluid. A detailed examination of failure rates expected in a geothermal power plant would complement the extensive corrosion research. Control methods could then be identified for the pipe locations where failures will most likely occur.

SECTION 2

INTRODUCTION

BACKGROUND AND PURPOSE

The recovery of energy from liquid-dominated geothermal systems involves large liquid flow rates. Geothermal fluids may be corrosive and may contain high concentrations of dissolved constituents, many of which are toxic. The operational and accidental releases of the geothermal fluid to ground water are of particular concern. The effects of the ground water pollution may be difficult to detect. Because of the very low flow velocities associated with ground waters, they are not readily flushed and once contaminated they may remain so. Direct discharge to surface water may be prohibited by state law as in California. For these reasons this study is directed toward ground water contamination.

Geothermal resources are commonly found in seismically active regions, where the geologic formations are highly fractured, providing avenues for contamination. Even in zones where geologic confinement appears adequate, slow migration of conservatively behaving constituents may pollute water supplies for future generations. If contamination can be predicted then mitigative action can be taken.

This report describes a methodology to identify potential ground water contamination at geothermal energy development sites. The procedure was developed to determine where significant impacts on ground water may occur as a result of operational or accidental releases. The objective is to provide a set of tools (e.g., graphical and analytical procedures) with data requirements and typical values which may be used at any site.

The methodology designed and presented here is for liquid-dominated systems. They are more abundant and conversion technologies are being developed. Analytical methods have been selected which have minimal data requirements, so that the methodology can be used in the early stages of site selection and development. Extensive temporal and spatial data are not required.

This report describes the screening methodology. Geothermal systems are described first (Section 3). Emphasis is on geothermal fluid characteristics and modes of potential releases to the ground water. The methodology is then presented (Section 4) with data requirements and analytical tools. Several example cases are given to demonstrate the use of the methodology. Limitations of the methodology are discussed including difficulties in obtaining reliable data. Typical data values for soil characteristics, adsorption coefficients, and numerical functions are included in the appendices.

USES OF THE METHODOLOGY

The methodology can be used as a regulatory tool by the EPA and state agencies and as a preliminary impact analysis tool by the geothermal development companies and electric utilities. As a regulatory tool the methodology can be used to identify the modes of release and locations where significant impacts on ground water may occur. Thus, potential geothermal power plant sites can be evaluated and recommendations for any needed mitigation measures made before full-scale commercial development takes place. The suggested mitigating measures can then be tested to determine their adequacy. Another use of the methodology by regulatory agencies might be to perform sensitivity analyses on various site-specific parameters to identify areas where problems might occur in developing monitoring programs.

The geothermal developer can use the methodology to predict potential impacts on ground water at a given site using the proposed plant design. The analysis would show where the most significant impacts may be expected. Appropriate control measures can then be tested using the methodology. This analysis may identify areas where a more detailed impact investigation is warranted. By performing the detailed analysis only where necessary, costs can be lowered and investigative effort can be allocated according to needs. Prior preliminary assessment of significant impacts may also be helpful to the developer and utility in estimating costs of the plant and in formulating maintenance schedules.

SECTION 3

DESCRIPTION OF GEOTHERMAL SYSTEMS

OVERVIEW OF EXISTING SITES

Liquid-dominated geothermal resources have been found in many of the western states and comprise a major part of the exploitable geothermal potential. This handbook has been prepared specifically to assist in the investigation of contamination potential from electrical generating plants using those resources. Only high temperature resources (>150°C) are considered. Table 1 summarizes features of some major development sites and gives installed electric generating capacity. Known Geothermal Resource Areas (KGRA) in the United States are shown in Figure 1. KGRAs where power generation is planned or currently conceived as possible are Niland, Heber, and East Mesa, California; Raft River, Idaho; Brady's Hot Springs, Nevada; Roosevelt Hot Springs, Utah; and Valles Caldera, New Mexico. Projected geothermal development for power generation is shown in Table 2.

Plant Design

The type of power plant which can be used in a liquid-dominated resource area depends on the temperature of the resource, the steam/water ratio, and the salinity. Three types are now being tested - direct flash, binary cycle, and hybrid, although the flash type is the only type now in commercial operation (not in the U.S.). Other types based on total flow are in the experimental stage (e.g., helical screw expander, impact turbine). Sketches showing components of each type of plant are shown in Figure 2. The flash cycle is most effective for high temperature resources with low to moderate salinity. The fluid can be flashed at successively lower pressures to recover additional heat. Binary cycle plants are suited for moderate to high temperature resources. The more common working fluids are isobutane and isopentane. The major advantage of the binary type of plant is that the turbine is isolated from the geothermal fluid by heat exchangers. However, dissolved solids can result in scale buildup in the heat exchangers and a loss of heat transfer efficiency. Hybrid plants use combined cycles to maximize heat recovery. Total flow turbines are being designed as an alternative to the conventional types for use in high dissolved solids resource areas but they have not yet proven feasible.

Site Characteristics

Many of the promising sites for development of geothermal power generation are in semiarid regions. Water availability is an important factor. For example, both the Imperial Valley region of California and the Raft River

TABLE 1. CHARACTERISTICS OF PRINCIPAL GEOTHERMAL FIELDS

Field	Reservoir temp. °C	Reservoir fluid	Average well depth (m)	TDS (ppm)	Installed capacity (MWe)
Larderello, Italy	245	Steam	1,000	<1,000	365
The Geysers, Calif.	245	Steam	2,130	<1,000	608
Matsukawa, Japan	230	Steam	1,100	<1,000	27
Otake, Japan	200+	Water	500	4,000	13
Wairakei, N. Zealand	270	Water	1,000	12,000	160
Broadlands, N. Zealand	280	Water	1,300	--	--
Kamchatka, USSR	200	Water	600	3,000	6
Cerro Prieto, Mexico	300+	Water	1,500	∿15,000	75
Niland, Calif.	300+	Brine	1,300	260,000	--
Ahuachapan, Salvador	230	Water	1,000	10,000	30*
Hvoragerdi, Iceland	260	Water	800	∿1,000	32 by 1980
Reykjanes, Iceland	280	Brine	1,750	∿40,000	--
Namafjall, Iceland	280	Water	900	∿4,000	3
Roosevelt, Utah	171	Water	850	7,000	--
Beowawe, Nevada	243	Water	3,000	1,200	--
Brady's Hot Springs, Nevada	193	Water	1,500	2,500	--
Brigham City, Utah	204	Water	3,300	54,000	--
Coso Hot Springs, California	227	Water	150	5,750	--
Long Valley, California	227	Water	350	1,500	--
Chandler, Arizona	178	Water	3,000	60,000	--
Clear Lake, California	186	Water	1,500	Low	--
Fly Ranch, Nevada	171	Water	300	Low	--
Mountain Home, Idaho	194	Water	3,000	800	--
Steamboat Springs, Nevada	193	Water	550	Low	--
Raft River, Idaho	149	Water	1,800	<2,000	--
Surprise Valley, California	171	Water	1,400	Low	--
Baca Ranch (Valles Caldera), New Mexico	260-315	Water	2,288	<4,000	--

*Under construction.
∿Approximate.

Source: Jet Propulsion Lab, 1975 and Public Service Company of New México, 1978

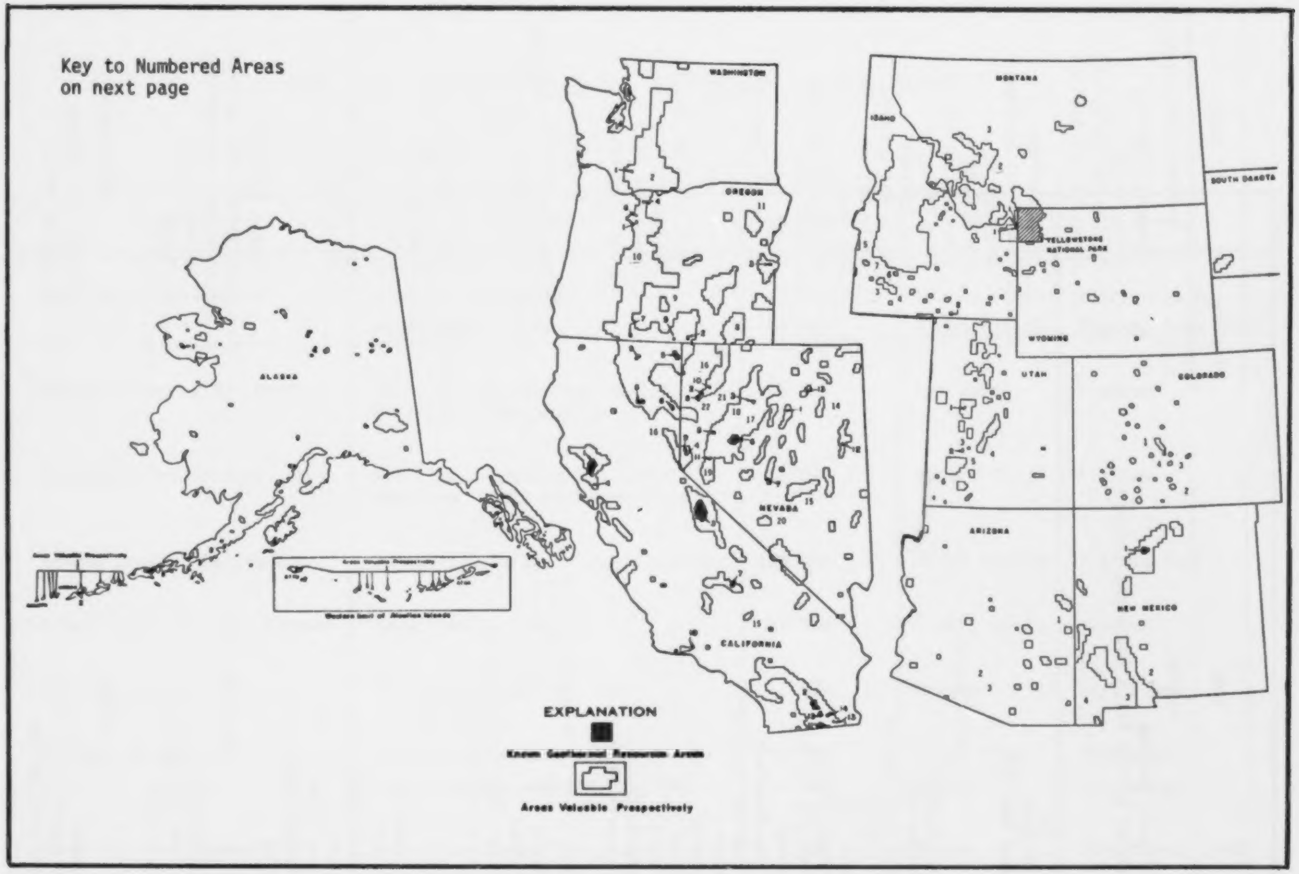

Key to Numbered Areas
on next page
WASHINGTON
OREGON
IDAHO
MONTANA
SOUTH DAKOTA
YELLOWSTONE NATIONAL PARK
WYOMING
UTAH
COLORADO
NEVADA
CALIFORNIA
ARIZONA
NEW MEXICO
ALASKA
Areas Valuable Prospectively
Western part of Aleutian Islands
EXPLANATION
Known Geothermal Resource Areas
Areas Valuable Prospectively

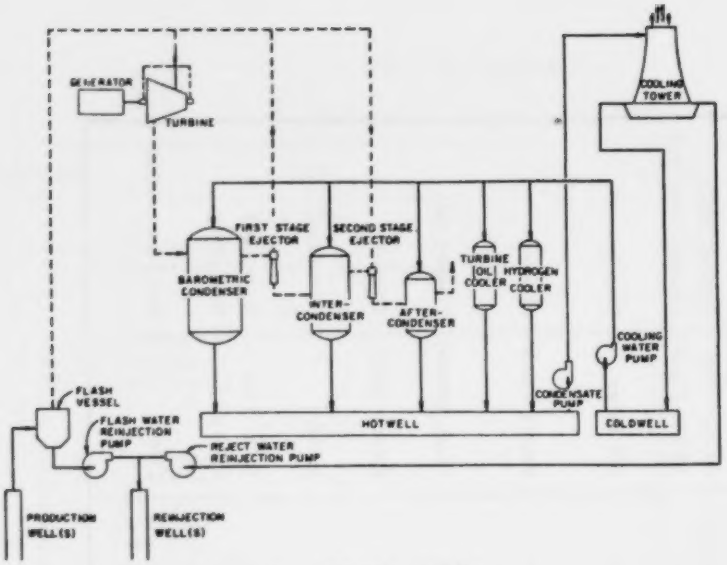
Figure 1. Map of known geothermal resource areas and geothermal exploration sites (After U.S.G.S., 1971; Koenig, 1975; Geothermal Resources Council, 1976 and National Geophysical and Solar-Terrestrial Data Center, 1977).

Key to Figure 1.

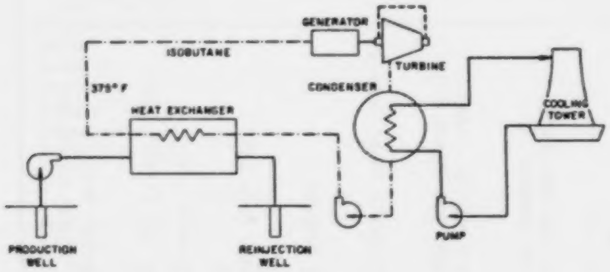
Locality	Name
	Alaska
1	Pilgrim Springs
2	Geyser Spring Basin and Okmok Caldera
	Arizona
1	Clifton
2	Chandler
3	Casa Grande
	California
1	The Geysers
2	Salton Sea
3	Mono-Long Valley
4	Calistoga
5	Lake City
6	Wendel-Amedee
7	Coso Hot Springs
8	Lassen
9	Glass Mountain
10	Sespe Hot Springs
11	Heber
12	Brawley
13	Dunes
14	Glamis
15	Randsburg
16	Beckworth Peak
	Colorado
1	Poncha
2	Alamosa
3	Valley View Hot Springs
4	Mineral Hot Springs
	Idaho
1	Yellowstone
2	Frazier
3	Castle Creek
4	Bruneau
5	Crane Creek
6	Mountain Home
7	Boise
	Montana
1	Yellowstone
2	Boulder Hot Springs
3	Marysville
	Nevada
1	Beowawe
2	Fly Ranch
3	Leach Hot Springs
	Nevada (Continued)
4	Steamboat Springs
5	Brady-Hazen
6	Stillwater-Soda Lake
7	Darrough Hot Springs
8	Gerlach
9	Moana Springs
10	Double Hot Springs
11	Wabuska
12	Monte Neva
13	Elko Hot Springs
14	Ruby Valley
15	Warm Springs
16	Pinto Hot Springs
17	Dixie Valley
18	Rye Patch
19	Wilson Hot Springs
20	Silver Peak
21	Trego
22	San Emidio Desert
	New Mexico
1	Baca Location No. 1
2	Radium Springs
3	Kilbourne Hole
4	Lightning Dock
	Oregon
1	Breitenbush Hot Springs
2	Crump Geyser
3	Vale Hot Springs
4	Mount Hood
5	Lakeview
6	Carey Hot Springs
7	Klamath Falls
8	Alford
9	Summer Lake Hot Springs
10	Belknap Foley Hot Springs
11	La Granda
	Utah
1	Crater Springs
2	Roosevelt Hot Springs
3	Cove Fort Sulphurdale
4	Monroe-Joseph
5	Thermo
6	Lund
	Washington
1	Mount St. Helena
2	Indian Heaven

TABLE 2. PROJECTED U.S. GEOTHERMAL POWER PLANTS

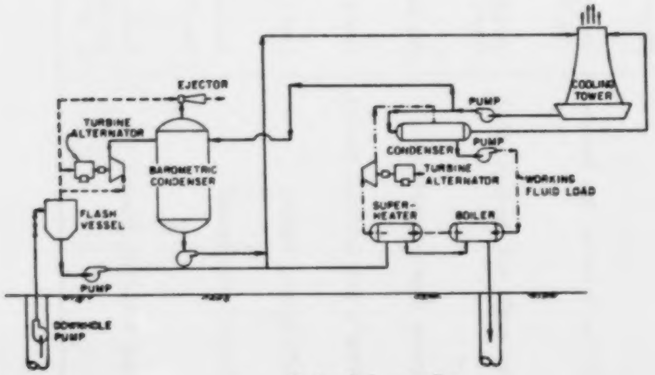
Location	Developer	Size	Type	Status
East Mesa, California	Republic Geothermal	48 MWe(Net)	Double flash	Planned 1980
	Magma Power, Inc.	10 MWe	Single flash	Planned late 1979
Valles Caldera, New Mexico	Union Oil Co. and New Mexico Public Service Company	50 MWe	Hot water	Planned
Roosevelt Hot Springs, Utah	Phillips Petroleum Co., Utah Power and Light and Rogers Int'l.	52 MWe	Double flash	Planned
Sonoma County, California	Northern California Power Agency	110 MWe	Flash (steam)	Planned 1981
Brady's Hot Springs, Nevada	Magma Energy Company	10 MWe	Binary cycle	Planned
Raft River, Idaho	Idaho Nat. Eng. Res. Lab	5 MWe	Binary	Test plant
Niland, California	Lawrence Livermore Lab	10 MWe	Total flow	Test plant
	San Diego Gas and Electric Co.	10 MWe	Binary	Test plant
Puna District, Hawaii	Hawaii Geothermal Project and Hawaii Electric Light Co. of Hilo	5 MWe	Flash	Test plant, 1980


GENERATOR
TURBINE
COOLING TOWER
FIRST STAGE EJECTOR
SECOND STAGE EJECTOR
BAROMETRIC CONDENSER
INTER-CONDENSER
AFTER-CONDENSER
TURBINE OIL COOLER
HYDROGEN COOLER
COOLING WATER PUMP
CONDENSATE PUMP
FLASH VESSEL
FLASH WATER REINJECTION PUMP
REJECT WATER REINJECTION PUMP
HOTWELL
COLDWELL
PRODUCTION WELL(S)
REINJECTION WELL(S)

a. Flash cycle


GENERATOR
ISOBUTANE
TURBINE
375° F
CONDENSER
HEAT EXCHANGER
COOLING TOWER
PUMP
PRODUCTION WELL
REINJECTION WELL

b. Basic isobutane cycle


EJECTOR
TURBINE ALTERNATOR
BAROMETRIC CONDENSER
FLASH VESSEL
PUMP
DOWNHOLE PUMP
COOLING TOWER
PUMP
CONDENSER
PUMP
TURBINE ALTERNATOR
WORKING FLUID LOAD
SUPER-HEATER
BOILER

KEY:

— Water

--- Steam

-.- Working fluid

c. Hybrid cycle

Figure 2. Sketches of general power plant cycles (a. after Huber _et al_, 1975; b. after Chou _et al_, 1974; c. after TRW, 1974).

region of Idaho are irrigated agricultural areas. Surface spills could be detrimental to crops. In the vicinity of some sites the ground water is used for irrigation and for public drinking water supply. Subsurface injection of spent geothermal fluid may protect surface waters, but care must be taken to avoid contamination of water supply aquifers.

The geologic setting of several geothermal sites is described in Table 3. The table shows that sites may be located on or near fault zones. Potential damage from earthquakes must be considered as well as movement of geothermal fluid or ground water along faults. Faults can act as conduits or as barriers. Landslides may be triggered by earthquakes, potentially causing damage to a geothermal site.

Site characteristics such as soils and type of geologic formations are varied (see Table 3). Since the methodology was designed for general use no site-specific data on soils were collected. Instead typical soil characteristics such as mineral composition, size analysis, permeability, and porosity were compiled and are included in Appendix B.

FLUID CHARACTERISTICS

Geothermal fluids are quite variable between sites and even within a reservoir as shown by the ranges and typical values for most major and minor components (Figure 3). Components of noncondensable gases are shown in Figure 4. Partitioning of the gases between fluid and steam phases at several sites is presented in Table 4. For this study chemical data from wells and springs in the U.S., Mexico, and New Zealand were collected. A summary of the data is listed in Table 5. These data were then compared to U.S. drinking water (see Table 26) and irrigation standards to determine constituent concentrations which exceeded the standards. Table 6 lists the constituents that exceed standards at one or more sites. Constituents which can cause scaling or corrosion problems in the plant and thus contribute to failures (accidental releases), including calcium carbonate, silica, and sulfate, were added to the list.

Using the chemical data collected, worst and typical case fluid chemistries were selected. It was felt that an example case should be based on one area to insure chemical compatibility and a more realistic scenario. Geothermal fluid from the Salton Sea area, California, was selected to represent a worst case fluid chemistry. East Mesa, California with much lower total dissolved solids, was selected as the typical case. For comparison purposes the worst case values anywhere are shown in Tables 7 and 8.

To demonstrate the environmental consequences of spills, comparisons were made between geothermal fluid concentrations and drinking water and aquatic life standards. Drinking water could be affected by the heavy metal concentrations and nitrate levels. The separate effects of constituents of geothermal fluids on freshwater and marine aquatic life are illustrated in Table 9. Cushman, et al. (1978) investigated the bioaccumulation by fish of elements present in geothermal fluids (Table 10). The Salton Sea area fluids were directly toxic to the fish. For the East Mesa fluids, accumulations in

TABLE 3. GEOLOGIC SETTING OF SELECTED CALIFORNIA KNOWN GEOTHERMAL RESOURCE AREAS

Location	Geologic setting	Reservoir rock	Faults
Coso Hot Springs	Volcanic flows overlain by Coso formation	Perlitic domes	E-W tension, some strike-slip
Calistoga	Alluvium underlain by Pliocene Sonoma volcanics	Basalt, andesite, rhyolite	N-S complex
Geysers	Franciscan metamorphics to Pleistocene lake beds	Metamorphic rocks	NW trend, numerous
Glass Mtn	In old caldera, rhyolitic obsidian flows	Lava flows	Limited
Lake City	Thick sediment with interspersed volcanics	Alluvium and volcanics	Surprise Valley fault
Lassen	Basaltic then rhyolitic lava flows and sediments	Volcanics	Some faulting in area
Mono Basin	Depression surrounded by Cenozoic volcanics	Volcanics	Bordering area
Long Valley	Quaternary volcanics (Basalts and rhyolites)	Volcanics	Postulated faults
Sespe Hot Springs	Mesozoic granitic rocks	Granite	Mutau & Pine Mountain Fault
Wendel-Amedee	Pliocene lake deposits (5,000') near Mesozoic granite rocks	Lake sediment	Faults act as conduits
Imperial Valley			
East Meas Heber Brawley Dunes Salton Sea	Sediment basin, faulted rift zone	Partly cemented sandstone & shale	Numerous en echelon faults

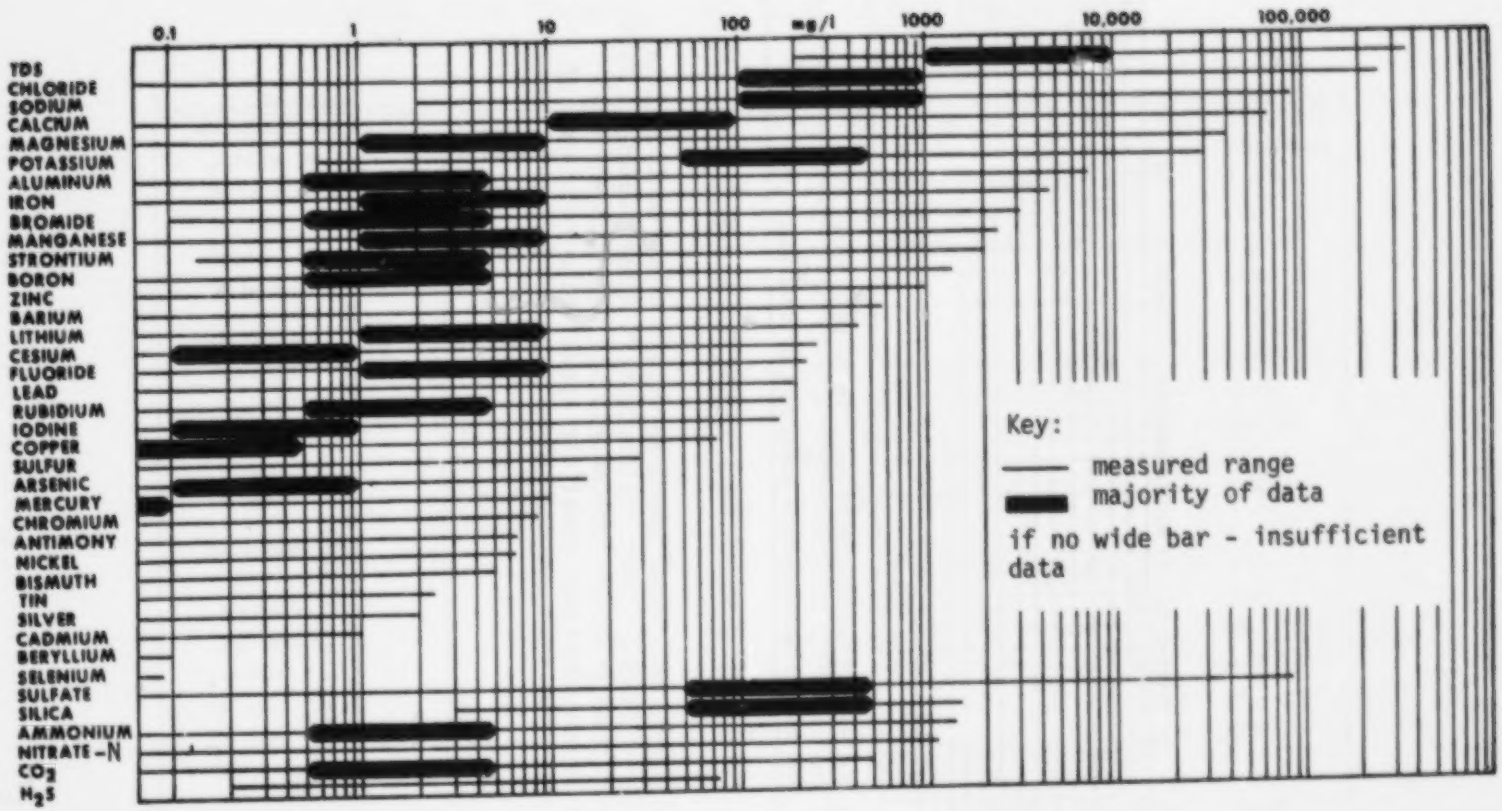
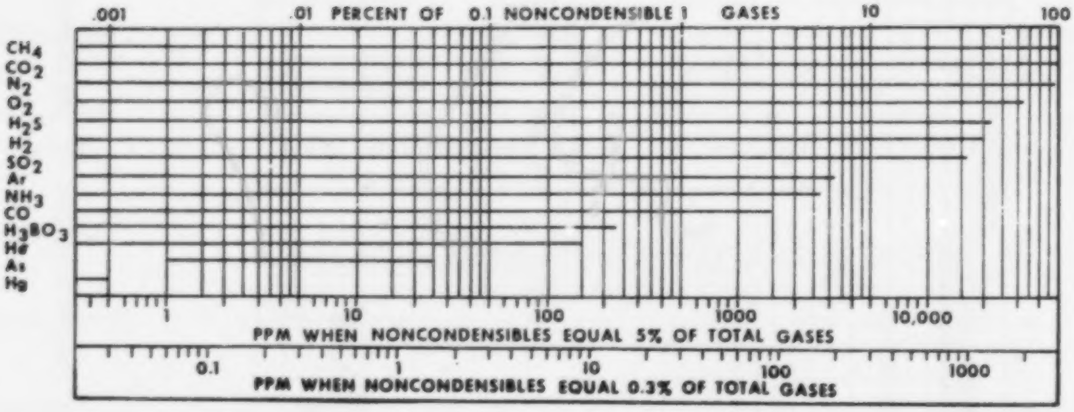


Figure 3. Ranges of chemical constituent concentrations in geothermal fluids (Hartley, 1978).



Note: Base graph shows individual gases as ranges of percent of total noncondensible gases. Lower scales convert these values to parts per million (ppm) of total (noncondensible plus condensible) gases when noncondensibles equal the specified percentages of total gases.

Figure 4. Noncondensible gases in geothermal fluids (Hartley, 1978).

TABLE 4. CONCENTRATIONS OF VARIOUS CONSTITUENTS IN GEOTHERMAL NONCONDENSIBLE GASES, STEAM CONDENSATES AND BRINE TO SHOW PARTITIONING BETWEEN PHASES

Constituents	Geothermal sites								
Non-condensible gases	The Geysers	Raft River	Vermillion Bay	East Mesa	East Mesa	Niland	Niland	Heber	Cerro Prieto
H_2S (ppm) VOL.	28,400-57,400	215	0.5-5	580-630	380	1390-1620	4670	--	15,000-20,000
Hg (µg/ℓ)	1.5-5.8	0.039	<0.001	2.3-3.6	3.3	0.8-1.6	1.8	<0.03	0.3-0.4
NH_3 (µg/ℓ)		--	130	108	--	45	--	--	17.8
Rn(pCi/)	3,820-27,800*	--	10-40	280-305	1095-1262	830-1150	535-644	3,200-4,300	--
As (µg/ℓ)	<0.003	--	--	--	--	--	--	--	<0.016
Steam condensate									
H_2S (mg/ℓ)	49-225	0.66	--	2.8	0.09	5.5	9.5	--	36-71
NH_3 (mg/ℓ)	157-818	1.8	--	98	15.5	331	360	--	88-163
Hg (µg/ℓ)	2.8-10	0.13	--	14.4	1.45	2.20	3.12	3.9	3.8-5.4
B (mg/ℓ)	6.4-76	<0.1	--	<0.1	--	5.9	--	<0.1	<0.1
As (mg/ℓ)	0.0014-0.092	0.012	--	--	--	--	--	--	0.006
Flashed brine									
NaCl (%)	--	0.13	10.4	1.77	--	16.5	--	--	2.27
H_2S (mg/ℓ)	--	0.1	--	0.33	0.07	--	--	--	0.16
NH_3 (mg/ℓ)	--	0.27	90	6.5	1.4	394	400	--	127
Hg (µg/ℓ)	--	0.022	0.007	0.003	<0.001	0.020	0.11	0.44	0.049
B (mg/ℓ)	--	0.13	40	9.8	--	340	--	--	19
As (mg/ℓ)	--	0.028	0.045	--	--	--	10.0	--	0.50-2.3
Ratio: $\frac{\text{Noncondensibles (ℓ)}}{\text{Steam (kg)}}$	1.96-4.46	0.25	1.6**	17.7	4.54	8.8	9.27	--	9.7
Brine flow (kg/hr)	--	--	--	10,600	--	109,000	--	7,500	1.58×10^6
Steam flow (kg/hr)	--	--	--	860	--	13,600	--	--	7.37×10^5
Temperature (°C) (incoming)	--	--	--	151	--	165	204	161	--
Date sampled	10/75, 5/76	7/76	5/77	3/77	9/77	5/77	9/77	3/77	5/76

*Radon Data from the Geysers by Stoker and Kruger, 1973 and by Anspaugh, *et al.*, 1977.

**No steam was produced. This is the ratio of noncondensible gas to brine in ℓ/kg.

after Robertson, *et al.*, 1978

TABLE 5. SUMMARY OF CHEMICAL ANALYSES OF GEOTHERMAL FLUID BY GEOGRAPHICAL AREAS (mg/ℓ except for pH and specific conductivity)

	States					KGRA'S			Foreign Sites	
Parameter	New Mexico median	Eastern Idaho average	West and Central Idaho average	Nevada average	Washington average	Salton Sea, CA average	East Mesa, CA average	Heber, CA average	Cerro Prieto, Mexico average	New Zealand average
TDS	1,112.0	3,385	320	1,850		207,639	4,422	14,493	17,000	
Sp. Cond., umhos/cm	550.0	4,398	763				12,082			
pH, units	7.7									
Aluminum	0.14					63	0.03	9		
Ammonia	0.1					424	12.6			3.8
Antimony	0.032					3	1.7			70
Arsenic	0.0			14		10	0.15			3.1
Barium				177		386	2.9	4		
Bicarbonate	163.0	310	127			1,663	389	20		
Boron	0.39					369	4.3	5.4		
Bromide	0.62			126		76	0.24			4
Cadmium							<0.02			
Calcium	37.6	91	8	20	82	23,746	165	935	362	8.2
Carbonate	0.0	2.8	22				0.4		2	
Carbon dioxide		5.8						4		
Cesium				153		20	0.75			1.1
Chloride	155.0	1,475	14		385	133,991	2,760	8,212	13,378	1,354
Chromium							<0.01		<0.05	
Copper	0.006					4.7	<0.10	0.4	0.005	1.3
Fluoride	3.0	3.2	7.9			3.2	1.9	1.3		6.6
Hydrogen sulfide						10-30				9
Iodide	0.023					14.5				0.5
Iron	0.14			182		1,895	1.2	10		
Lead	0.08					102	0.4	0.8	0.005	1
Lithium	0.3				1.3	198	9.2	4.2		7.5
Magnesium	6.9	80.6	2.3		22.2	481	4.2	7.9		0.20
Manganese				37	0.13	1,026	0.28	1.3		0.001
Nickel	0.01						0.11		0.002	0.7
Nitrate		2.6	0.6			275	0.19			

(continued)

TABLE 5 (continued)

Parameter	States					KGRA'S			Foreign sites	
	New Mexico median	Eastern Idaho average	West and Central Idaho average	Nevada average	Washington average	Salton Sea, CA average	East Mesa, CA average	Heber, CA average	Cerro Prieto, Mexico average	New Zealand average
Phosphate	0.05						<0.1			
Potassium	10.0	171.5		22	25.8	13,595	177	238		130
Rubidium				174		110				1.3
Selenium	0.0						0.5			
Silica	50.0	56	66	133.5	116	217	207	222		628
Silver						1	0.01		0.004	
Sodium	167.0	865	75	228	353	51,268	1,619	4,614	6,234-5/7	842
Strontium					0.37	454	83	37		
Sulfate	81.0		35			119	125	130		37
Sulfide		167				25	1.5			
Tin	0.0			48		23	<0.01		0.4	
Zinc	0.026					672	<0.02			1.5
Scandium				0.04						
Tungsten				72			<0.1			
Uranium				0.18				<4		
Molybdenum				5.4			<0.005			
Titanium							<0.1			
Mercury							0.006			
Tantalium							0.13			
Cobalt							0.03			
Beryllium							<0.02			
Bismuth							0.6			
Niobium							0.4			
Germanium							<0.1			
Vanadium							0.005			

Note: Data were compiled from many sources, including unpublished data, and are included in the list of references. Blank spaces indicate that no data were available.

TABLE 6. CHEMICAL CONSTITUENTS OF INTEREST IN GEOTHERMAL FLUIDS

Constituent	Location of potential problems
TDS	Average value exceeds standard everywhere but Idaho.
Aluminum	Problem* in CA sites.
Ammonia	Problem in CA sites.
Arsenic	Problem in Salton Sea, East Mesa, and Nevada.
Barium	Problem in CA and Nevada.
Boron	Problem for irrigation.
Cadmium	Problem in East Mesa, but only place with data.
Chloride	Average value exceeds standard at all places but west and central Idaho, New Mexico and Nevada.
Chromium	Problem in some areas although limited data available.
Copper	Problem at Salton Sea and Niland.
Fluoride	Problem at Salton Sea and sites in New Mexico and Idaho.
Copper	Problem at Salton Sea and Niland.
H_2S	Problem at Niland.
Iron	Problem at all sites.
Lead	Problem at all sites with data.
Lithium	Problem at Salton Sea, East Mesa, and Niland.
Magnesium	Problem only at Salton Sea.
Manganese	Problem at CA sites.
Selenium	Problem at East Mesa, very little data.
Silver	Problem in CA sites.
Zinc	Problem in CA sites.
Mercury	Data for East Mesa exceeds standard, no data anywhere else.
Molybdenum	Data for Nevada exceeds irrigation standards.
Sodium	Harmful for irrigation uses at most sites.
Nitrate	Problem in some CA sites, Idaho, and New Mexico.

*A potential problem exists whenever a drinking water or irrigation standard was exceeded.

TABLE 7. GEOTHERMAL FLUID CONCENTRATIONS FOR PROBLEM CONSTITUENTS (mg/ℓ)

Constituent	Worst case, Salton Sea	Worst case at any site	Typical case, East Mesa	Lowest at any site
Aluminum	450	450	0.03	0.0
Ammonia	570	570	12.6	0.1
Arsenic	15	40	0.15	0.025
Barium	1,100	1,100	2.9	0.15
Boron	745	745	4.3	0.0
Cadmium*	<0.02	<0.02	<0.02	<0.02
Chloride	210,700	210,700	2,760	0.0
Chromium	No data	<0.05**	No data	<0.5
Copper	10	10	<0.1	0.0
Fluoride	18	24	1.9	0.0
H_2S	No data	30	No data	No data
Iron	3,416	3,416	1.2	0.0
Lead	200	200	5	0.0
Lithium	400	400	9.2	0.0
Magnesium	2,225	2,225	4.2	0.0
Manganese	4,000	4,000	0.28	0.02
Nitrate	1,050	1,050	0.19	0.0
Selenium*	1.8	1.8	0.5	0.0
Silver	1.0	1.0	0.01	0.01
Zinc	970	970	0.02	0.006
Mercury	0.014	0.014	0.006	0.002
Molybdenum*	0.005	0.005	0.005	0.005
Sodium	78,000	78,000	1,619	0.4
TDS	387,500	387,500	4,422	10
Temperature, °C	188-332	-	309-399	-
pH	3.9-7.5	-	5.4-7.1	-
Pressure, psig	220-445	-	$\sim$60	-

*Data available only at East Mesa.

**Data available at Cerro Prieto, Mexico.

TABLE 8. GEOTHERMAL FLUID CONCENTRATIONS OF ADDITIONAL CONSTITUENTS

Constituent	Worse case, Salton Sea	Worse case at any site	Typical case, East Mesa	Lowest at any site
Bicarbonate	6,900	6,900	389	0.0
Bromide	146	720	0.31	0.0
Calcium*	40,000	40,000	165	0.1
Carbonate*		175	4	0.0
Cesium		340	0.75	0.14
Chromium***	<.01†		<0.01	
Iodide	22	22	no data	0.0
Nickel	0.16†	0.16†	0.11	0.0
Phosphate			<0.1	
Potassium	29,900	29,900	177	0.0
Rubidium	168	174	40††	40††
Silica*	625	625	207	0.1
Strontium†††	740	740	83	0.1
Sulfate*	621	5,190	125	0.0
Sulfide	30	1,052	1.5	0.3
Tin	23 (only 1 value)	180	<0.01	<0.01
Uranium	<4†††	<4†††	0.02††	0.02††
Tungsten	150††	150††	<0.1	<0.1

*Constituents of interest for corrosion and scaling problems.

†Data only at East Mesa.

††Data at Nevada.

†††Data for Heber only.

TABLE 9. AQUATIC LIFE CRITERIA

Constituent	Criteria level for fresh water	Criteria level for marine water	Remarks
Ammonia (un-ionized)	0.02 mg/l		Toxicity pH dependent
Arsenic		0.05 mg/l	Daphnia impaired by 4.3 mg/l
Aluminum		1.5 mg/l	
Barium			Toxcity level <50 mg/l
Beryllium	0.11 mg/l (soft water) 1.1 mg/l (hard water)		Toxcity hardness dependent
Boron			Toxic to minnows at 19,000 mg/l
Cadmium	.004 - .0004 mg/l (soft water) .012 - .0012 mg/l (hard water)	0.005 mg/l	Toxic at <0.5 mg/l all tests
Chromium	0.1 mg/l		Toxicity varies with pH and oxidation state
Chlorine	0.003 mg/l	0.003 mg/l	
Copper	0.1 96-hr LC$_{50}$	0.05 mg/l	Toxicity alkalinity dependent
Cyanide	0.005 mg/l	0.01 mg/l	
Iron	1.0 mg/l		Toxicity variable
Fluoride		1.5 mg/l	
Lead	0.01 96-hr LC$_{50}$ (sol. lead)	0.05 mg/l	Salmonids most sensitive fish
Manganese		0.1 mg/l	Not a problem in fresh water
Mercury	0.0005 mg/l	0.0001 mg/l	High bio-accumulation and thus affects human food
Nickel		0.1 mg/l	
Nitrates			Toxicity to fish >900 mg/l
Phosphorus		0.0001 mg/l P	Eutrophication factor
Selenium	0.01 96-hr LC$_{50}$	0.01 96-hr LC$_{50}$	Toxic at >2.5 mg/l
Silver	0.01 96-hr LC$_{50}$	0.01 96-hr LC$_{50}$	Toxicity dependent on compound
Hydrogen sulfide	0.002 mg/l	0.005 mg/l	Toxic at very low concentrations
Zinc	0.01 96-hr LC$_{50}$		Toxicity dependent on temperature, dissolved oxygen, hardness
Total dissolved solids (TDS)			Osmotic effects - variable

Source: U.S. EPA, 1977 and Federal Water Pollution Control Administration, 1968

TABLE 10. RELATIVE HAZARDS OF GEOTHERMAL FLUIDS

Element	TC[a] (mg/l)	BF for fish	DWS (mg/l)	TBC (33DWS/BF) (mg/l)	Ratios					
					Salton Sea		East Mesa		Salton Sea	East Mesa
					Conc./TC	Conc./TBC	Conc./TC	Conc./TBC	Conc/DWS	Conc/DWS
As	0.022	333[b]	0.05[d]	0.005	818	-	7	-	360	3.2
B	0.069	1[c]	1[e]	33	1,285	-	6.6	-	887	4.6
Ba	5.3	4[b]	1[d]	8.25	247	-	.6	.4	1,309	3.1
Br	0.18	417[b]	3.0[f]	0.24	967	-	1.8	1.4	58	0.11
Cr	0.005	4,000[b]	0.05[d]	0.0004	4	-	4	-	0.4	0.4
Cu	0.0006	200[b]	0.1[f]	0.02	20,000	-	166	-	600	0.1
Fe	0.2	100[b]	0.3[g]	0.10	20,335	-	6.5	-	13,557	4.3
Hg	0.0001	1,000[b]	0.002[d]	0.0001	170	-	60	-	8.5	3
Mn	0.35	660[b]	0.05[g]	0.003	13,606	-	.86	100	95,240	6
Ni	0.03	100[b]	0.05[f]	0.02	6	-	4	-	3.8	2.4
Pb	0.007	300[b]	0.05[d]	0.006	34,000	-	771	-	34,000	108
Rb	14.0	2,000[b]	5[f]	0.08	14	-	3	-	40	8.6
Ti	2.0	1,000[b]	0.1[f]	0.003	-	-	-	-	-	-
Zn	0.01	8,500[b]	5[g]	0.02	115,500	-	2	-	231	.004

[a] Cushman, Hildebrand, Strand, and Anderson (1977b)

[b] Thompson, et al. (1972)

[c] Thompson, et al. (1976)

[d] Federal Register (1976)

[e] Federal Water Pollution Control Administration (1968)

[f] Dawson (1974)

[g] U.S.P.H.S. (1962)

Source: After Cushman, et al., 1977a

Note:

BF = Bioaccumulation factor
DWS = Drinking water standard
TC = Toxic concentration to fish
TBC = Threshold bioaccumulation concentration

fish of barium, bromide and manganese could occur. This study does not give hazards for specific kinds of fish and thus is approximate but it does indicate the risk of indiscriminate discharge of geothermal fluids.

Some states, including California, have prohibited discharge of geothermal fluids to surface water because of the toxicity of some constituents to aquatic life and agricultural crops. An accidental release to irrigation water could result in crop-damaging concentrations of boron, heavy metals, and total dissolved solids (Table 11).

TYPES OF FLUID RELEASES

Failure Modes

Operating experience in the U.S. with geothermal power plants is limited to 15 years with the steam-driven power plants at The Geysers, California. Failure modes have been derived from that experience and from experience with similar power plant components. A general summary of types of failures and probable causes is shown in Table 12. A review of the known geothermal plant failures in California (Table 13) shows that all the possible types have occurred. A study on energy-related accidents made by the EPA (1977) considered a well blowout to be a potential major accident. A summary of known geothermal well blowouts is given in Table 14. This summary suggests that the probability of blowouts may be significant. Pipe failures have been investigated in more detail although the probability estimates should be considered preliminary only.

Pipe Failures

Pipe failures include pressure-induced rupture due to scale blockage, and leakage due to corrosion, abrasion, or improper connections. Table 15 summarizes the plant operating history for several foreign plants using liquid-dominated resources to show scale and corrosion problems. In reviewing data from geothermal plants one should realize that generally low grade materials are used (Yasutake and Hirashima, 1970; Bechtel, 1976; Tolivia, *et al*., 1970). Listed below are examples of materials used:

Components	Materials
• Piping	mild steel, high chromium alloy, carbon steel
• Well casing	carbon steel
• Turbine	titanium alloy, low chromium alloy
• Heat exchanger tubes	titanium alloy
• Condenser	304 stainless steel and epoxy-coated carbon steel

TABLE 11. AGRICULTURE USE CRITERIA FOR CONSTITUENTS IN GEOTHERMAL FLUIDS (EPA, 1976)

Constituent	Crop irrigation	Remarks
Ammonia		No criteria suggested.
Arsenic	0.1 mg/l	Toxicity to some crops at 0.5 mg/l; no livestock criteria suggested.
Barium		No criteria suggested.
Beryllium	0.001 to 0.5 mg/l	Crop toxicity acidity dependent; no livestock criteria suggested.
Boron	0.75 mg/l	Toxic to sensitive plants, e.g., citrus at <1 mg/l; no livestock criteria suggested.
Cadmium		Reduced crop yields at 1 mg/l; crop accumulation related to zinc concentrations; no livestock criteria suggested.
Chromium		No criteria suggested.
Copper		Toxicity for plants begins at 0.1 mg/l; no livestock criteria suggested.
Iron		No criteria suggested.
Lead		Toxic to plants at <30 mg/l; no criteria suggested.
Manganese	0.2 mg/l suggested for acidophilic crops	Toxicity to plants increases with decreasing pH; no livestock criteria suggested.
Mercury		Bioaccumulation, but no criteria suggested.
Nitrates		No criteria suggested; nutrient for crops.
Phosphorus		No criteria suggested; nutrient for crops.
Selenium		No criteria suggested.
Silver		No criteria suggested.
Hydrogen sulfide		No criteria suggested.
Zinc		Toxic to some crops at 0.4 to 25 mg/l; may cause iron deficiency in plants; no livestock criteria suggested.
Total dissolved solids	500-1,500 mg/l suggested	Osmotic effects in plants; variable harm to both plants and animals.
Sodium		Toxic to certain plants; ratio to other cations important; no criteria given.

TABLE 12. FAILURE MODES AND MECHANISMS OF HYDROTHERMAL SYSTEM COMPONENTS

Component	Failure mode	Estimate of relative probability	Mechanisms of failures	Factors responsible
Well casings	Blowout, crack	Low	Stress corrosion, erosion, plugging up of casing perforations and geological formations	High H_2S, temperature, pressure, and TDS
Valves	Jammed in open or close position	Moderate	Scaling, plugging	TDS
Pipes	Leak, rupture	High	Scaling Pitting and erosion (elbows) Embrittlement, then stress corrosion	TDS, H_2S Pressure at elbows, particulates
New well	Blowout	Moderate low	Clogging, loss of control of well	High TDS, high pressure
Injection well	Blowout	Low	Plugging of perforations, injection formation	Particulates, bacteria, TDS, aeration
Storage ponds	Overflow Leak	Moderate Moderate	Spill Break in liner	Flow rates exceed capacity Acidity, differential settling

TABLE 13. SUMMARY OF HISTORICAL GEOTHERMAL FAILURES IN CALIFORNIA

Type	Area	Date	Break location	Spill amount	Likely cause
Surface	Niland	6/16/74	Reinjection pipe, 1/4 x 3" hole	1,000 gal.	Crack in pipe
Surface	East Mesa	12/4/76	Wellhead	16,000 gal.*	Jammed valve, 3/4" open for four hours
Surface	Heber	4/29/76	Injection wellhead	1,000 gal.*	Unknown
Surface	Brawley	1/16/76	Separator line	Small amount went to lined pit	Plugged line for 2-3 min.
Surface	Casa Diablo	78?	Well	Unknown	Blowout during test
Surface	The Geysers	9/10/71	Cooling tower pipe	∿20,000 gal. to Big Sulfur Creek	Pipe failure
Surface	The Geysers	9/9/74	Steam condensate pipe	∿4,500 gal.	Mechanical failure
Surface	The Geysers	2/28/75	Condensate pipe	∿10,000 gal.	Break - unknown cause
Surface	The Geysers	6/6/75	Condensate pipe	∿3,000 gal.	Break - unknown cause
At depth	Niland	76?	Casing in well	Unknown	Pressure, had no production liner

*Water was first dumped to a lined sump pit then reinjected later.

∿ = approximate.

Source: California Department of Fish and Game, 1976 and California Regional Water Quality Control Board, 1978

TABLE 14. KNOWN WELL BLOWOUTS

Location	Number of blowouts/ number of wells	Time period
The Geysers, CA	4/100 (4%)	1957-1978
Beowawe, Nevada	3/11 (due to vandalism)	1959-1965
Cesano and Lardarello, Italy	Several	-
Cerro Prieto, Mexico	2/40 (5%)	1961,1972
Wairakei, New Zealand	3/100 (3%)	-
Dieng, Java	1	1978

Source: Sung, *et al.*, 1978; TRW, 1976; and Geothermal Resources Council, 1978

TABLE 15. HISTORY OF SELECTED GEOTHERMAL PLANTS

Location	Plant type	Hours of operation	Damage	Location of damage
Otake, Japan	Single cycle	8,700	None in plant	Pipeline flow cut in half by scale
Matsukawa, Japan	Single cycle	Approx. 8,700	Scale, 20% decrease in flow	Pipes
		Unknown	Collapsed well casing	Well was killed with 150,000 tons of cold water
Kamchatka, USSR	Single cycle	5,000	None	--
Otake, Japan	Single cycle	51,900	10 kg SiO_2, FeS sludge	Receiving tank
			SiO_2 scale	Strainer in steam pipe
			3-4 mm Fe oxide scale +SiO_2	Turbine
			.1-.2 mm rust	Turbine blades
			1 mm S tray, cracks	Condenser
			Some concrete corrosion,<1 mmS on pipe, blisters on coating	Hot water tank
Niland test plant	Single cycle	700	SiO_2+$CaCO_3$ scale	Pipes

Source: Yasutake and Hirashima, 1970, and Uchiyama and Matsuura, 1970

Note: Fluid releases may not have occurred at these plants as a result of the damage.

• Valves	carbon steel
• Hot water tank	stainless steel, chromium-molybdenum steel

The nature of the brine may make corrosion a serious problem at geothermal power plants. Corrosion rates are site- and material-dependent. In general, factors which influence corrosion rates include pH, dissolved oxygen, chloride, and H_2S concentrations and temperature. The variability of rates between selected sites is shown in Figure 5.

Corrosion data from geothermal fluid testing and plant experience were obtained from a literature survey. The tests were conducted in actual geothermal fluids or in specified sodium chloride solutions. Table 16 gives selected test results for actual geothermal fluids. Using these corrosion rates and typical pipe sizes, comparative estimates of failure rates due to uniform corrosion and pitting were calculated (Table 17).

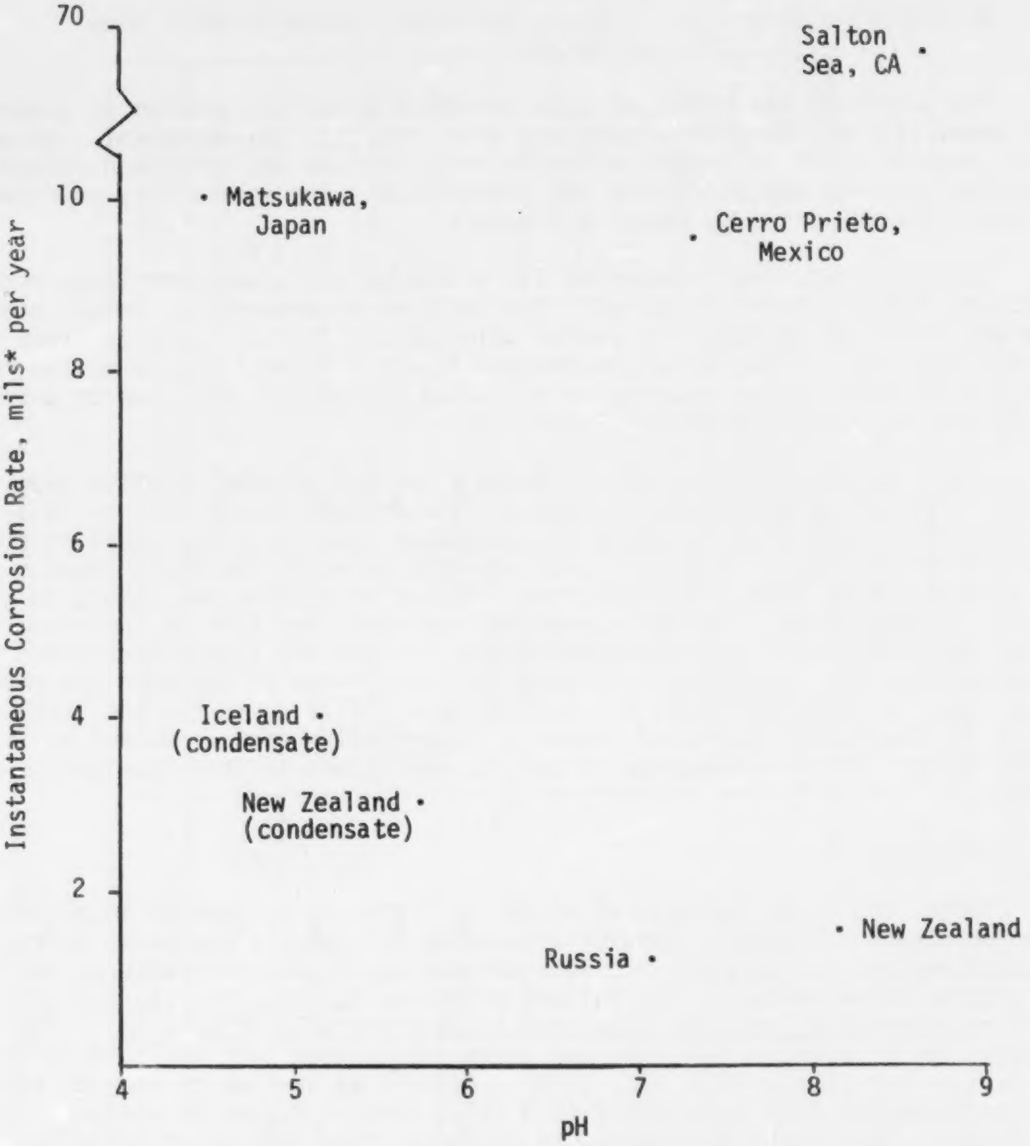
These calculated rates are not exact rates but do show relative magnitudes. Failure is a stochastic process. The probability of failure in a long section of a given pipe is likely to be greater than in a very short section. Failure probability is higher in sections of pipe where the fluid impacts on it directly as in pipe elbows and tees. Higher velocities may result in higher failure rates. The calculated failure rates may also be low since other mechanisms such as erosion-corrosion, fatigue and stress corrosion cracking were not considered. Uniform corrosion tends to decrease the endurance limit as shown in Figure 6. Methods to minimize corrosion are listed in Table 18. Geothermal corrosion research is currently being conducted by several investigators. Knowledge of control mechanisms is thus expected to increase.

Valve Failures

Valves can cause failure and allow fluid release by jamming in either the open or closed positions. Opening or closing too quickly may cause excessive impact pressure and rupture. Failure to open may cause overpressures and lead to pipe or valve rupture. The failure of valves to close may cause spills such as occurred at the East Mesa site in California (see Table 13). The probability of a valve rupturing was estimated between 10^{-7} and 10^{-9} failures/hr for nuclear plants (U.S. AEC, 1975). Failure of a valve to open or operate was estimated as 10^{-6} failures/hr (U.S. AEC, 1975). Valves in contact with geothermal fluid could be expected to jam more often because of scale buildup. A comparison of reactor cooling water and typical geothermal fluid is presented in Table 19. The differences in water chemistries suggest that the probability of valve failure is perhaps an order of magniture higher for geothermal fluids, although detailed valve specifications were not available from which to make a more exact estimate.

Pond Leaks

Several types of ponds may be located at a geothermal site such as temporary storage ponds to contain fluid while repairs are being made, settling



*1 mil = 0.0254 mm.

Figure 5. Corrosion rate of 1010 mild steel in geothermal fluids of varying pH (after Bechtel, 1976).

TABLE 16. CORROSION RATES OF MATERIALS IN GEOTHERMAL FLUIDS

Material	Type of fluid/location		Uniform corrosion rate mm/yr	Maximum pitting rate, mm/yr
Aluminum	Aerated steam, S	CP		2.9
Aluminum	Condensate, H	CP	.48	3.65
Carbon steel	Aerated steam, S	CP	.44	
Carbon steel pipeline	Steam	M	0.636	
Low carbon steel	Condensate, H	CP	.66	
Epoxy coated carbon steel	Condensate	M	.0084	
Deoxidized copper	Aerated steam, S	CP	1.11	
Deoxidized copper	Condensate, H	CP	0.64	
1 Cr-1 Mo-.25V	Aerated steam, S	CP	.5	
1 Cr-1.25 Mo-.25V	Steam	M	.623	
12 Cr steel	Aerated steam, S	CP	.14	1.7
12 Cr steel	Condensate, H	CP	.09	.97
High cr alloy	Concentrated brine	SS	.125	
12 Cr-XAl steel	Steam	M	.049	
12 Cr-.2Al	Aerated steam, S	CP	.16	
12 Cr-1 Mo-1W	Aerated steam, S	CP	.23	1.6
15 Cr-1.7 Mo$^+$	Aerated steam, S	CP	.023	1.2
Mild steel	Concentrated brine	SS		1.75
Naval brass	Condensate, H	CP	.22	
Ni alloy	Concentrated brine	SS	<.025	
3.5 Ni-1.75 Cr-.5 Mo-.12	Aerated steam, S	CP	.52	0.7
Stainless steel	Concentrated brine	SS	<.025	
18-8 Stainless steel	Condensate, L	CP	.0008	
304 Stainless steel	Condensate	M	.0212	
410 Stainless steel	Steam in turbine	M	.0213	

Sources: Tolivia, et al., 1970, and Yasutake and Hirashima, 1970

Notes: CP = Cerro Prieto, Mexico; M = Matsukawa, Japan; SS = Salton Sea;
H = velocity of 0.5 m/sec; L = velocity of 0.02 m/sec;
S = velocity of <140 m/sec.

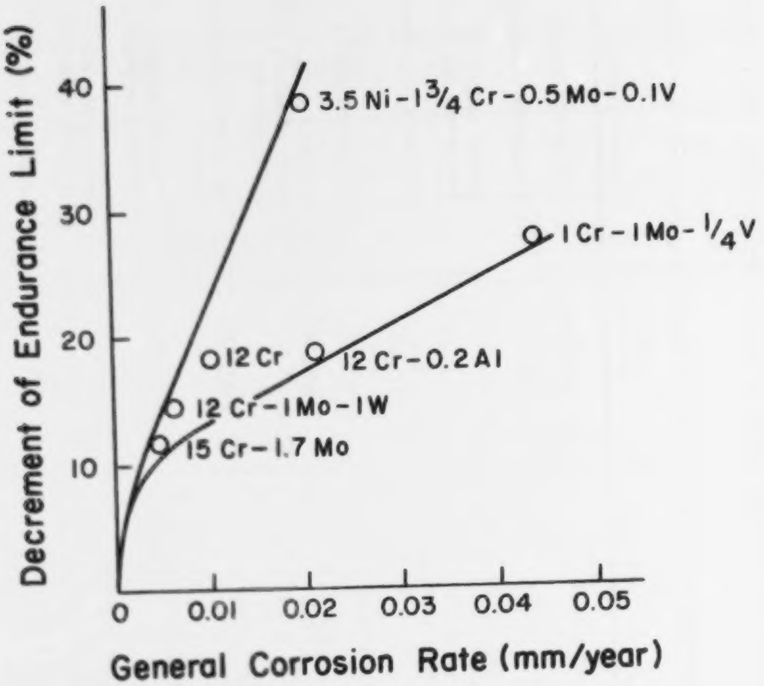
TABLE 17. CALCULATED FAILURE RATES FOR PIPES

Well to separator		Wall	Uniform corrosion	Maximum pitting	Corrosion* failure rate	Pitting** failure ate
Material	Diameter, cm	thickness, mm	rate mm/yr	rate mm/yr	failures/hr	failures/hr
Low carbon steel	114.3	19.05	.66	1.75	4×10^{-6}	1.0×10^{-5}
	86.4	15.9	.66	1.75	4.7×10^{-6}	1.3×10^{-5}
	76.2	12.7	.66	1.75	5.9×10^{-6}	1.6×10^{-5}
	61.	17.4	.66	1.75	4.3×10^{-6}	1.1×10^{-5}
	40.6	9.5	.66	1.75	7.9×10^{-6}	2.1×10^{-5}
	20.3	8.2	.66	1.75	9.2×10^{-6}	2.4×10^{-5}
High Cr	114.3	19.05	.125		7.5×10^{-7}	
	61.	17.4	.125		8.2×10^{-7}	
12 Cr steel	114.3	19.05	.09	.97	5.4×10^{-7}	5.8×10^{-6}
	61.	17.4	.09	.97	5.9×10^{-7}	6.4×10^{-6}
Ni alloy	114.3	19.05	.025		1.5×10^{-7}	
	61.	17.4	.025		1.6×10^{-7}	
18-8 Stainless steel	114.3	19.05	.0008		4.8×10^{-9}	
	86.4	15.9	.0008		5.7×10^{-9}	
	76.2	12.7	.0008		7.2×10^{-9}	
	61.	17.4	.0008		5.2×10^{-9}	
	40.6	9.5	.0008		9.6×10^{-9}	
	20.3	8.2	.0008		1.1×10^{-8}	
Steam pipes						
Aluminum	76.2	12.7	.095	2.9	8.5×10^{-7}	2.6×10^{-5}
Deoxidized copper	76.2	12.7	1.11		9.9×10^{-6}	
15 Cr-1.7 Mo	76.2	12.7	.023	1.2	2.1×10^{-7}	1.1×10^{-5}
12 Cr steel	76.2	12.7	.14	1.7	1.3×10^{-6}	1.5×10^{-5}

*Calculated from wall thickness/uniform corrosion rate = S,
1/S/hrs per year = failures/hr.

**Same except used pitting rate instead of corrosion rate.

Note: See Table 16 for type of fluid used in tests



Note: Tests were made in low velocity nonaerated steam

Figure 6. Effect of corrosion on fatigue for different alloys (after Tolivia, Hoashi, and Miyazaki, 1970).

TABLE 18. METHODS TO CONTROL CORROSION IN GEOTHERMAL FACILITIES

Equipment type	Cause of corrosion	Type of corrosion	Control methods
Well and wellhead	Acidic brines	Surface	Use carbon steels
Well and wellhead	High velocity	Erosion	Streamline conduits
Well casing, external	Aerated and/or acidic waters	Surface	Cement suited for geothermal applications
Turbine blades	Hydrogen sulfide	Stress and fatigue	Use low alloy steels
Pipelines	Acidic brines	Surface	Use carbon steels
Condensers, ejectors and cooling towers	H_2S and O_2	Surface	Minimize O_2 leakage, use H_2SO_4 resistant materials, neutralization
Structures	Spray	Surface	Use corrosion resistant materials
Packings	Air and brine	Surface	Minimize leakage, use resistant materials
Electronics	Hydrogen sulfide	Tarnish	Exclude H_2S, use resistant materials
Pipelines in standby mode	Air and brine	Surface	Exclude air

Source: After Jet Propulsion Lab, 1975

TABLE 19. CHARACTERISTICS OF NUCLEAR COOLING WATER AND GEOTHERMAL FLUIDS

Constituent	Typical range of geothermal fluid*	Typical range of fluids in nuclear power plant	
		Primary coolant**	Reactor coolant makeup water**
TDS, ppm	1,000-10,000	.5	<0.5
Cl, ppm	100-1,000	0-0.15	0-0.15
F, ppm	1-10	0-0.1	0-0.1
DO, ppm at 25°C	--	<0.1	nondeaerated
Additives (Li, K, or NH_3)	--	<25	--
Max Boric Acid, ppm	.4-5 as B	<9800	--
pH	2-10***	4.5-10.2	6-8

*Hartley, 1978
**Considine, 1974
***Tsai, et al., in press

ponds for injection pretreatment, or ponds under the piping system to contain spilled fluid. Leakage can occur from overflow or seepage through the bottom. Overflow leaks can be minimized by proper sizing of the pond to contain, for example, one or two day's production flow rate of fluid plus the precipitation amount from a given frequency storm (e.g., 1 in 10 year storm). Ponds should meet appropriate regulations for disposal of hazardous waste (40 CFR 250). Ponds should be lined with clay or other impermeable material to minimize leakage. Some leakage may still occur, so the ground water flow regime and distance to nearby surface waters should be considered before siting the pond.

SECTION 4

DESCRIPTION OF METHODOLOGY

GENERAL PROCEDURE

This chapter comprises the "user's manual" for the methodology which provides a framework to identify potential ground water contamination problems resulting from geothermal energy development at specific sites. The methodology is shown schematically in Figure 7 and includes the following steps:

- Determine environmental concerns
  - Are there usable aquifers in power plant site area?
  - Are aquifers interconnected?
  - What are present and potential uses?
  - What are concentrations of geothermal fluid constituents?
  - Do geothermal fluid concentrations exceed water quality standards?
  - Are geothermal fluids capable of mobilizing pollutants from the soil?
- Determine release potential
  - Where may releases occur?
  - What is probability of a release to surface or ground water?
  - How much fluid may be released?
  - What are physical and chemical characteristics of the released fluid?
- Identify potential ground water contamination
  - Can released geothermal fluid migrate to aquifers?

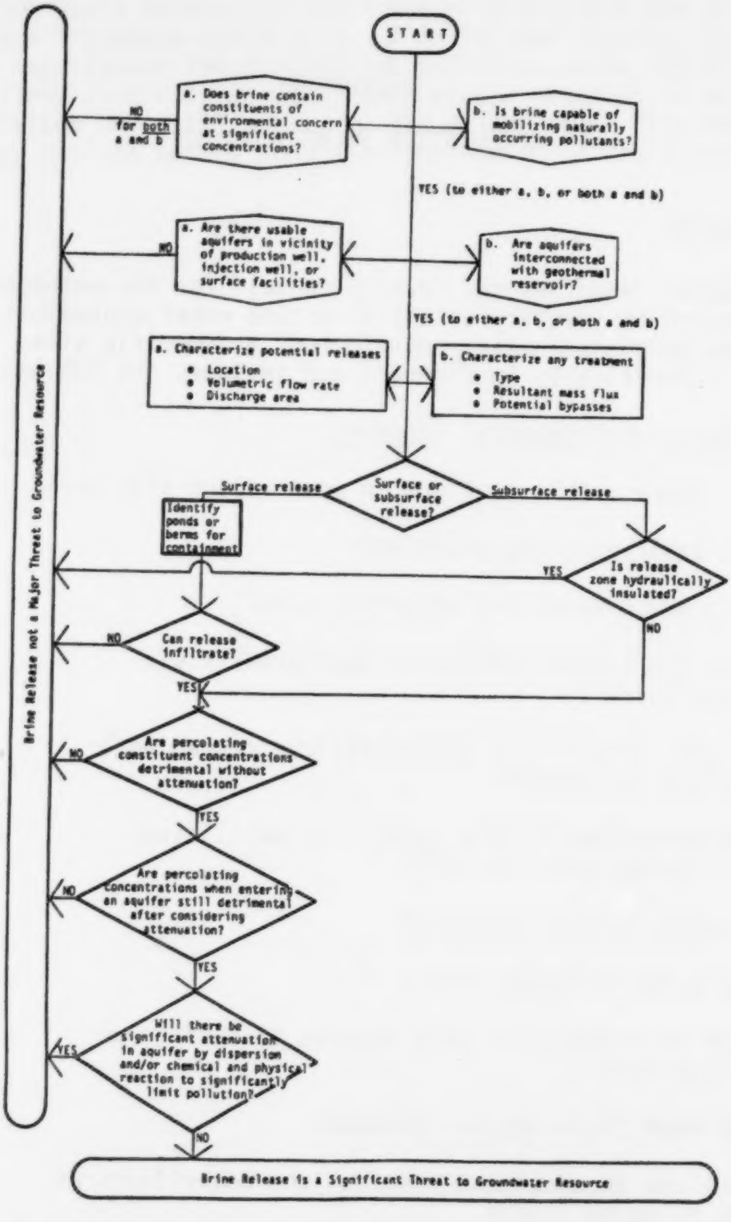

START
a. Does brine contain constituents of environmental concern at significant concentrations?
b. Is brine capable of mobilizing naturally occurring pollutants?
NO for both a and b
YES (to either a, b, or both a and b)
a. Are there usable aquifers in vicinity of production well, injection well, or surface facilities?
b. Are aquifers interconnected with geothermal reservoir?
NO
YES (to either a, b, or both a and b)
a. Characterize potential releases
• Location
• Volumetric flow rate
• Discharge area
b. Characterize any treatment
• Type
• Resultant mass flux
• Potential bypasses
Surface or subsurface release?
Surface release
Subsurface release
Identify ponds or berms for containment
Is release zone hydraulically insulated?
YES
NO
Can release infiltrate?
NO
YES
Are percolating constituent concentrations detrimental without attenuation?
NO
YES
Are percolating concentrations when entering an aquifer still detrimental after considering attenuation?
NO
YES
Will there be significant attenuation in aquifer by dispersion and/or chemical and physical reaction to significantly limit pollution?
YES
NO
Brine Release not a Major Threat to Groundwater Resource
Brine Release is a Significant Threat to Groundwater Resource

Figure 7. Steps of methodology.

- Are dilution and attenuation mechanisms adequate to prevent significant levels of contamination?

- Evaluate significance of contamination

The procedure applies a logical sequence of questions and analytical techniques to problem areas to identify those of most concern. The analysis moves to the next step only if a potential problem is identified. Each step has a set of associated specific methods. Data requirements, pertinent analytical tools, and examples for each step are discussed in the following sections.

ENVIRONMENTAL CONCERNS

The first part of the methodology is to identify the environmental concerns by answering the following questions outlined earlier:

- Are there usable aquifers in power plant site area?
- Are aquifers interconnected?
- What are present and potential uses of aquifers?
- What are concentrations of geothermal fluid constituents?
- Do geothermal fluid concentrations exceed water quality standards?
- Are geothermal fluids capable of mobilizing pollutants from the soil?

The first step is to locate all usable aquifers in the site area and to evaluate the extent of interconnectivity between the aquifers. Aquifers may be located from geologic maps and well logs of the area. Interconnections may be indicated or identified from water level data, pumping records, and knowledge of faults. The next step is to identify present uses and to estimate potential future uses of the aquifers. Existing uses can be determined by examination of water supply reports in the area or well permits. These are available from those states or local water resource agencies that require permits. In the Salton Sea area of southern California, for example, the aquifers are not used as drinking water sources at the present time but contamination of shallow ground water and surface spills could pose a threat to agriculture.

If the aquifers are used, the next step is to examine the concentrations of constituents in the geothermal fluid. The geothermal fluid concentrations at the site should be compared with appropriate water quality standards to determine if any standards are exceeded. (See Table 9 for aquatic life limits, Table 26 for drinking water standards, and Table 11 for agricultural use limits.)

Another concern is the possibility of spilled geothermal fluid mobilizing heavy metals present in the soil. Soil analyses can be used to identify constituents which can be desorbed or exchanged at the given pH range of the geothermal fluid. The low pH associated with some geothermal fluids can mobilize several heavy metals.

RELEASE POTENTIAL

The next major section of the methodology is to determine the release potential if the user has identified possible environmental concerns should a release of geothermal fluid occur. The steps are to determine:

- Where may releases occur?
- What is probability of a release to surface or ground water?
- How much fluid may be released?
- What are physical and chemical characteristics of the released fluid?

Release Points

The steps for locating potential releases are:

- Examine the power plant schematic in light of the potential release diagram (Figure 8)
- Locate places where releases are possible
- Identify likely failure modes
- Compare geothermal fluid at site with threshold values
- Check for mitigating features in plant design to prevent failure

Potential release points include:

- Pipes, flow lines
- Valves, separators, heat exchangers
- Production wells, and
- Injection wells.

The specific locations where accidental or operational releases may occur depend on the type and size of power plants and the fluid characteristics. Figure 8 presents a general diagram to locate potential releases. The diagram highlights the conditions which may lead to well blowouts and surface

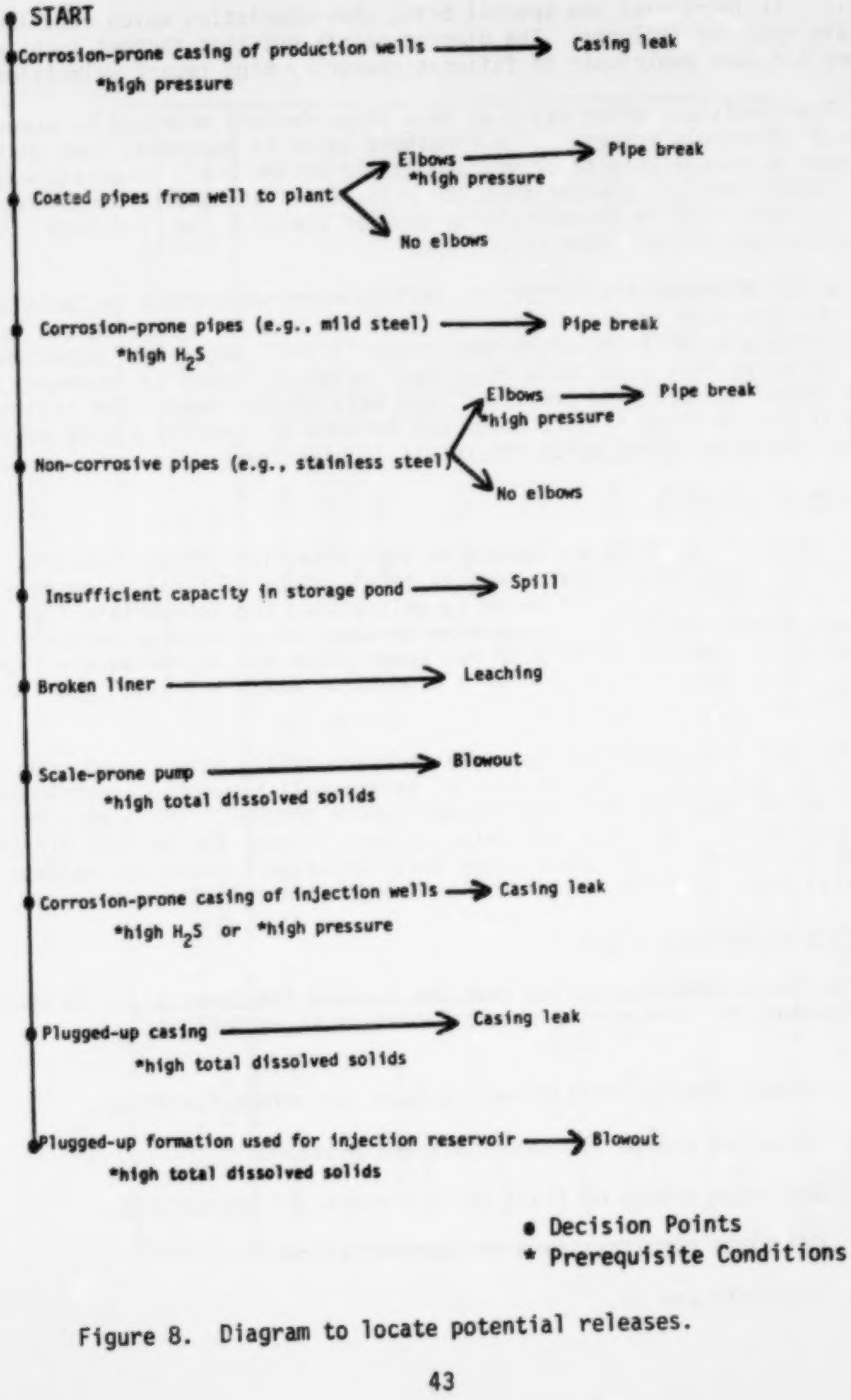

START
Corrosion-prone casing of production wells
Casing leak
*high pressure
Coated pipes from well to plant
Elbows
*high pressure
Pipe break
No elbows
Corrosion-prone pipes (e.g., mild steel)
Pipe break
*high H_2S
Non-corrosive pipes (e.g., stainless steel)
Elbows
*high pressure
Pipe break
No elbows
Insufficient capacity in storage pond
Spill
Broken liner
Leaching
Scale-prone pump
Blowout
*high total dissolved solids
Corrosion-prone casing of injection wells
Casing leak
*high H_2S or *high pressure
Plugged-up casing
Casing leak
*high total dissolved solids
Plugged-up formation used for injection reservoir
Blowout
*high total dissolved solids
● Decision Points
* Prerequisite Conditions

Figure 8. Diagram to locate potential releases.

spills. It identifies the special brine characteristics which contribute to certain types of failures. The diagram points out that factors such as pipe elbows and tees contribute to failures caused by high impact velocities.

The conditions which may lead to a given failure mode can be expressed in terms of threshold values. If a threshold value is exceeded, then that failure mode is more likely to occur. Threshold values are: temperature greater than 200°C, pressure greater than 100 psia, flow rate greater than about 10 m/s, hydrogen sulfide concentrations greater than 0.1 ppm, and total solids concentrations greater than 10,000 ppm.

Relative probabilities for the failure modes were given in Table 12. Other factors such as length of time plant has been in operation and maintenance procedures will influence the probabilities. Geothermal experience to date indicates that pipe leaks occur most often, followed in frequency by valve leaks, surface pond overflows, and well casing leaks. The information given in Section 3 on failure modes can be used to identify piping subject to high corrosion rates which can result in pipe leaks.

Quantity of Releases

Expected flow rates are needed at each potential release location identified in the above step. The potential total volume of fluid released at a specific location can be estimated by multiplying the appropriate flow rate by the anticipated operator response time to complete corrective action. Geothermal fluid flow rates for a 50 MWe power plant are approximately 10,400 gpm --total plant flow; 1,000 gpm--for a production well; and 2,000 gpm--for an injection well.

Operator response times to actual surface spills have ranged from three minutes to four hours. In the case of severe well blowouts, several days or months may be required to bring the well under control. Table 20 gives examples of probable flow rates and total release volumes for several different release locations. This table shows that the largest potential release volumes will most likely be associated with injection well failures.

Chemistry of Released Fluid

The fluid chemistry varies from one part of the power plant to another. The procedure for determining chemical changes is as follows:

- Obtain chemical data at well bottom (or before flashing),
- Calculate change in temperature and pressure,
- Determine amount of fluid which flashes, if appropriate,
- Calculate resultant chemical concentrations,
- Calculate new pH,

TABLE 20. VOLUME OF POTENTIAL RELEASES

Release location	Flow rate, gpm	Worst case		Typical case	
		Response time	Volume, gallons	Response time	Volume, gallons
Surface pipe	2,600*	4 hr	624,000	.5 hr	78 ,000
Surface valve	50	4 hr	12,000	.5 hr	1,500
Producing well blowout	1,000	1 day	1,440,000	2 hr	120,000
Injection well blowout	2,000	1 day	2,880,000	2 hr	240,000
Casing leak in producing well	100	4 hr	24,000	1 hr	6,000
Casing leak in injection well	200	12 hr	144,000	4 hr	48,000
Surface pond leak	1,500,000 gallon storage	Break in pond berm	1,500,000	Slow leak	Variable

*Based on one-fourth of total plant flow

- Determine likely precipitates using solubility diagrams, and
- Check the concentration of corrosive chemicals in solution.

Chemical data should be obtained by measurement. If site-specific data are not available for all constituents, values may be estimated from the data included in Section 3 (Table 6 "Average Chemical Data from Three KGRA's and Five States"). As an alternative, the worst and typical concentrations (Tables 8 and 9) may be used. Table 21 gives temperature, pressure, and pH changes from wellhead through the power plant outlet. These values were compiled from several power plant designs.

The next step is to determine changes in concentrations due to changes in temperature and pressure as the fluid moves from the production wells through the power plant to the surface ponds or injection wells. As the fluid moves up the well, the pressure drops, allowing the release of steam, carbon dioxide and other gases. This process, known as flashing, has a concentrating effect since most constituents remain in the liquid phase. As the pressure decreases the temperature also decreases. The concentration of certain fluid constituents may exceed their solubility limit at the lower temperatures and precipitate.

In a binary cycle plant or a total flow cycle plant the fluid would not flash but would decrease in temperature as it flowed from the wellhead to the heat exchangers or turbines. Precipitation may occur as the solubility limits of constituents are exceeded.

To determine the amount of fluid flashing at the wellhead. the volume of steam and liquid at the well site can be measured or estimated by a graphical technique. For the latter method Figure 9, which shows the percent of liquid flashing to steam versus temperature, can be used. Since the loss of water as steam concentrates the remaining constituents, the new concentrations are calculated based on the percent of remaining liquid. The new concentration can be calculated as follows:

$$C_n = C_o \div F \qquad (1)$$

where C_n = new concentration

C_o = original concentration

F = fraction of remaining fluid = $\left(1 - \frac{\text{percent of liquid flashed}}{100}\right)$

If the condensate re-enters the flow stream, concentrations may again approach those in the production well.

Often information on geothermal fluids does not include values for pH. Yet pH values are needed to predict the behavior of several heavy metals in permeable media. If concentration values are presented for bicarbonate and carbonate an estimate of the solution pH in equilibrium with atmospheric gases can be made.

TABLE 21. CHANGES FROM WELLHEAD TO PLANT OUTLET TEMPERATURE, PRESSURE AND pH

Plant type, size, and location	Wellhead to plant outlet temperature, °C	Wellhead to plant outlet pressure change, psia	Wellhead to plant outlet pH change
Flash at Heber, CA, 50 MWE	182-103		
Flash at Valles Caldera, New Mexico, 50 MWe	260-103		
Flash at Raft River, ID, 50 MWe	149-98		
Dual flash at Raft River, ID, 10.5 MWe	150-121-98	Est. 161-103, reinj. at 309	
2-Stage flash at East Mesa, CA, 50 MWe	180-104	57	7-9.8
Binary at Raft River, ID, 50 MWe	149-92	400	
Binary cycle at Raft River, ID, 10 MWe	150-110-71	Est. 161-103, reinj. at 309	
Binary at Valles Caldera, New Mexico, 50 MWe	260-45	600	
Binary at Heber, CA, 50 MWe	182-68	600	
Binary cycle (4 heat exchangers) 10 MWe	200-113	290	6.5-7.5
Hybrid at Heber, CA, 50 MWe	182-72		
Hybrid (2 stage) at Heber, CA, 50 MWe	182-67	312	6.2
Hybrid at Valles Caldera, New Mexico, 50 MWe	260-103		
Hybrid at Raft River, ID, 50 MWe	149-98		
Hybrid (2 stage) at Niland, CA, 50 MWe	230-67	840	5.1-5.6†
10 MWe design plant	177-120	140	

†Depends on amount of CO_2 gas and buffering capacity.

Source: Bechtel, 1976; TRW, 1974; and LBL, 1976

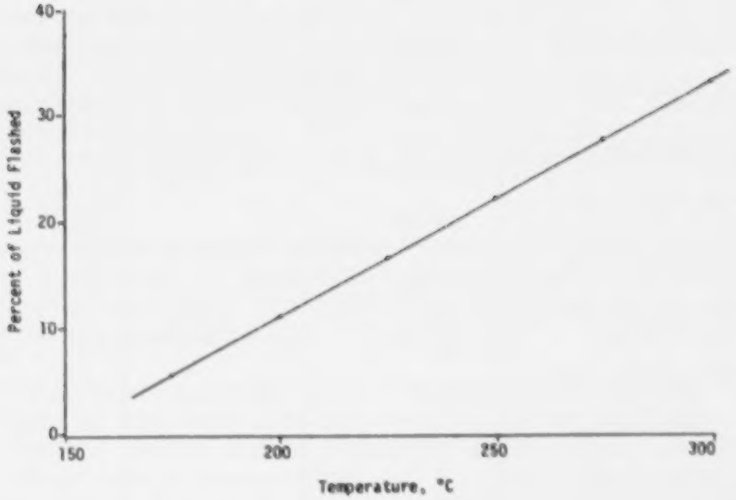


Figure 9. Liquid flashed versus temperature at atmospheric pressure (after Barr, 1975).

First the acid neutralizing capacity [ALK] of the solution is estimated:

$$[ALK] \cong [HCO_3^-] + [CO_3^{2-}] \qquad (2)$$

where [ALK] = alkalinity, meq/ℓ

$[HCO_3^-]$ = bicarbonate concentration, in meq/ℓ

$[CO_3^{2-}]$ = carbonate concentration, in meq/ℓ

The alkalinity value is then used in conjunction with Figure 10 to obtain an estimate of pH.

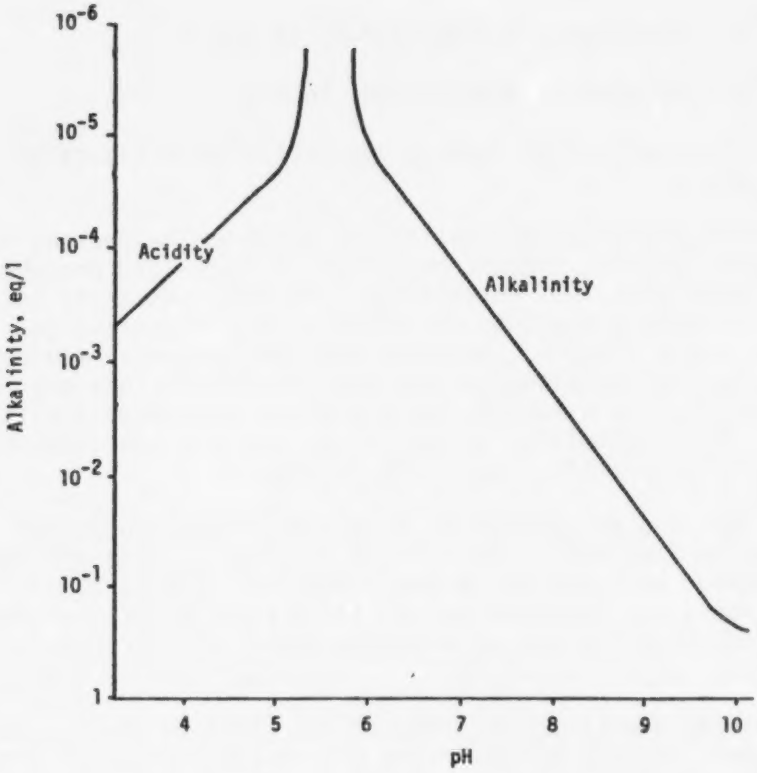
Other acid neutralizing constituents which may be present include silicates, borates, ammonia, organic compounds, sulfides and phosphates. At pH values less than about 8-9, borates and silicates contribute only slightly to the total alkalinity since they are almost fully protonated (e.g., $pK_{B(OH)3} \cong 9.2$ and $pK_{Si(OH)4} \cong 9.5$). The other substances usually add negligible amounts to the total alkalinity since these concentrations are relatively low. Acidity (dissociation) constants for the above substances are included in Appendix A. These calculated values for pH are only approximations. If measured values are available they should be used.

The pH may also be calculated using equilibrium expressions for the chemical species involved or equilibrium diagrams. These methods are described in detail by Stumm and Morgan, Chapters 3 and 4, 1970. The graphical method used above was selected because it is easy to use. If a more exact answer is needed equilibrium calculations with ionic strength corrections can be substituted.

Neutralizing agents may be added to the fluid to prevent corrosion or scale problems. Changes in alkalinity and pH after addition of neutralizing agents can be estimated using the alkalinity versus total carbonate diagram (Figure 11). The appropriate alkalinity and Ph contour for the fluid before addition of the neutralizing agents is first located on the figure. One then moves according to the small vector diagrams at the bottom of the figure to determine how the pH and/or alkalinity may change. This figure can be used for low to moderate alkalinity values.

The amount and type of precipitates found in wells and pipes depend on the chemical species present, the degree of supersaturation, temperature, and available surface area per unit mass of fluid (Rimstidt and Barnes, 1978). Table 22 shows the types of precipitates found at selected geothermal sites. Chemical species likely to precipitate may be identified from solubility diagrams. These diagrams may be constructed in several ways depending on whether solubility of the species is dependent on pH, temperature, or concentration.

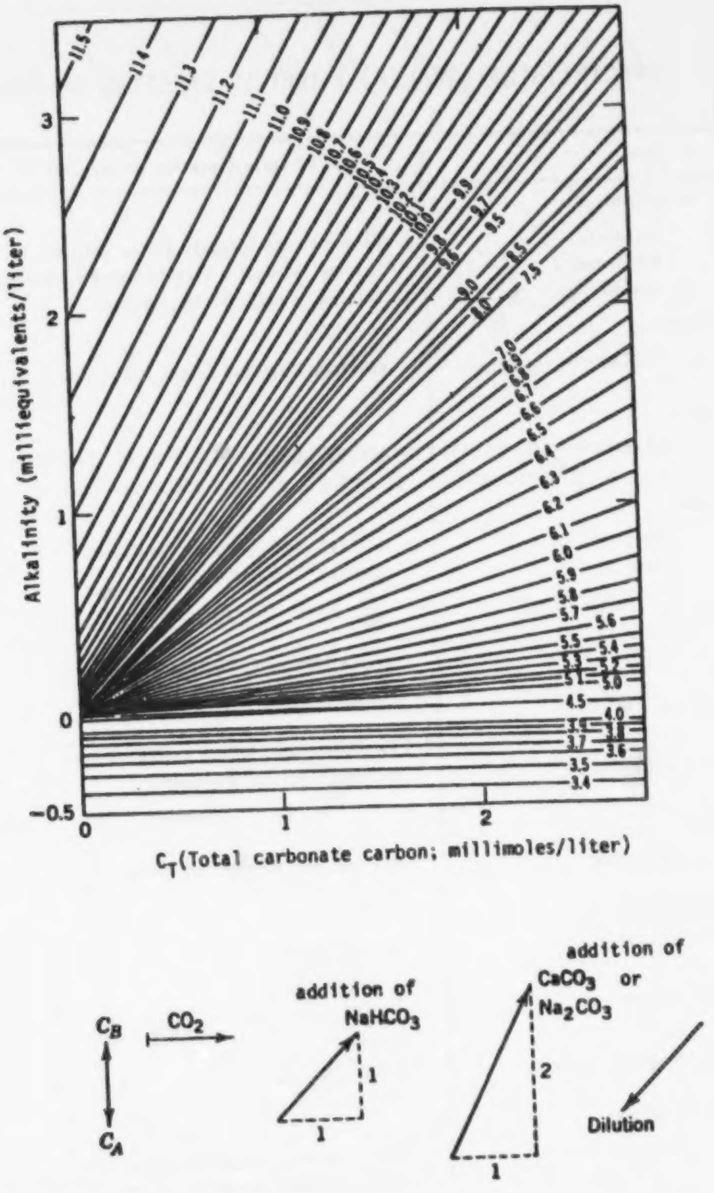
The concentrations of metal cations are typically pH-dependent. To determine if a metal carbonate or metal oxide-hydroxide precipitate may form, the concentration of the metal ion can be plotted on solubility diagrams (Figure 12a and 12b). The equilibrium concentration at different pH values is



Note: Other conditions were:

$\rho CO_2 = 10^{-3.5}$ atm, T = 25°C.

Figure 10. Alkalinity versus pH (After Stumm and Morgan, 1970).



C_A, addition of strong acid

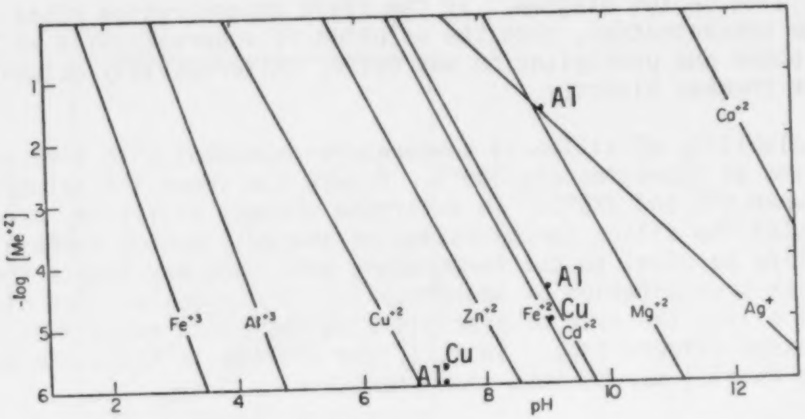
C_B, addition of strong base

Figure 11. Alkalinity versus total carbonate, showing pH contours (Stumm and Morgan, 1970).

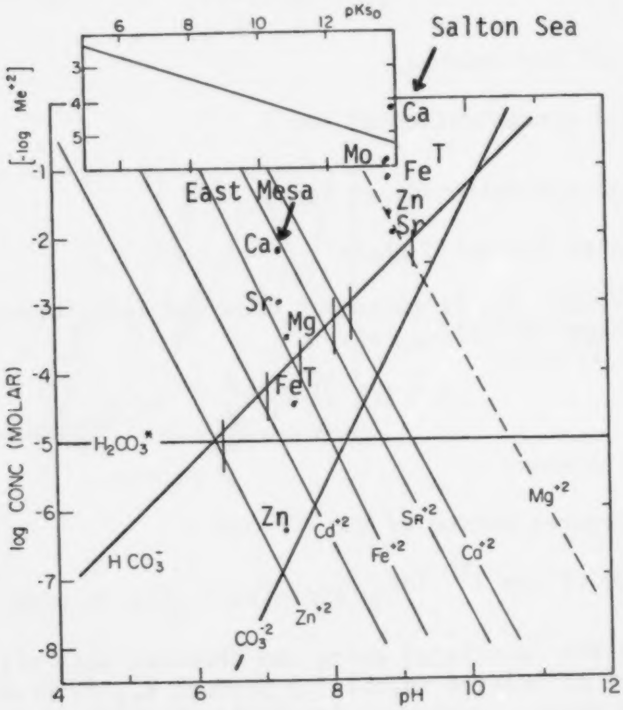
TABLE 22. PRECIPITATES (SCALES) FOUND AT EXISTING GEOTHERMAL SITES

Site	Type of scale (location of deposit)
New Zealand	
Wairakei	Minor calcite (pipes), silica (drains)
Broadlands	Calcite (pipes), silica (silencers, drains)
Kawerau	Calcite (pipes), silica (drains)
Turkey	
Kizildere	Calcite, aragonite (pipes and plant)
Chile	
El Tatio	Calcite (pipes)
Japan	
Matsukawa	FeO, FeS, $FeSO_4$, silica, sediments
Otake	Calcite, silica (drain pipes)
Taiwan	
Matsao	Silica, PbS, FeS, Pb (pipes)
Iceland	
Reykjavik	Fe oxides, MgO, silica (pipes, plant)
Namafjall	Amorphous silica, chalcedony
Italy	
Larderello	Silica, FeS, borates, silicates
Soviet Union	
Bolshe-Bannoe	Calcite (pipes)
Phillippines	
Tiwi	Calcite
Tongonan, Leyte	Aragonite
United States	
Steamboat Springs	$CaCO_3$, probably aragonite (pipes)
Casa Diablo	$CaCO_3$, probably aragonite (pipes)
Salton Sea	Silica, hydrated Fe oxides, metal sulfides (pipes and plant)
The Geysers	Siliceous material, rock dust (pipes and plant)
Mexico	
Cerro Prieto	Calcite, silica, Fe oxides (pipes, plant)

After Ellis and Mahon, 1977



a. Metal ion concentrations in equilibrium with solid oxides or hydroxides. Temperature = 25°C.



b. Free metal concentrations in equilibrium with metal carbonates. Vertical dash indicates equilibrium concentration with $pCO_2 = 10^{-3.5}$. Temperature = 25°C.

Figure 12. Examples of solubility diagrams (After Stumm and Morgan, 1970).

shown as a line on the diagram. If the fluid concentration plots above the equilibrium concentration, then the solution is supersaturated with respect to the solid phase and precipitation may occur. Alternatively solubility products can be checked directly.

The solubility of silica is temperature-dependent with a maximum solubility occurring at approximately 300°C. Figure 13a shows the solubility of silica between 0°C and 375°C. To determine whether silica may precipitate in the well, plot the silica concentration at the well bottom temperature. By drawing a line parallel to the temperature axis, one may locate the temperature at which precipitation of amorphous silica may begin. For high concentrations of silica the rate of precipitation decreases rapidly as the temperature decreases (Figure 13b). Thus, if the cooling is fast, the amount of precipitate (scale) may be less than predicted.

The solubility of concentration-dependent chemical compounds can be represented by thermodynamic constants called solubility products. For the reaction $AB(s)^* \rightleftharpoons A^+ + B^-$ the solubility product is written as:

$$K'_{sp} = A^+ \; B^- \tag{3}$$

where K'_{sp} = solubility product

A^+ = molal concentration of ion A

B^- = molal concentration of ion B

*(s), indicates the solid phase

The solubility product K'_{sp} is dependent upon the ionic strength of the solution. Ionic strength is defined as:

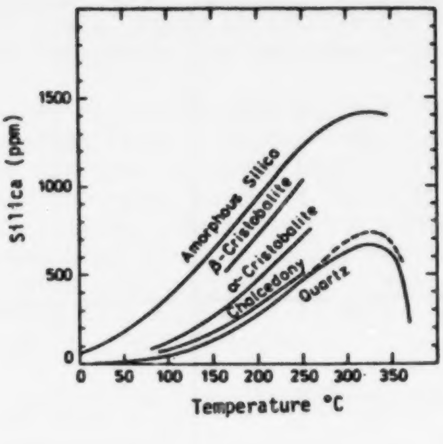
$$I = 1/2 \sum M_i \; V_i^2 \tag{4}$$

where I = ionic strength

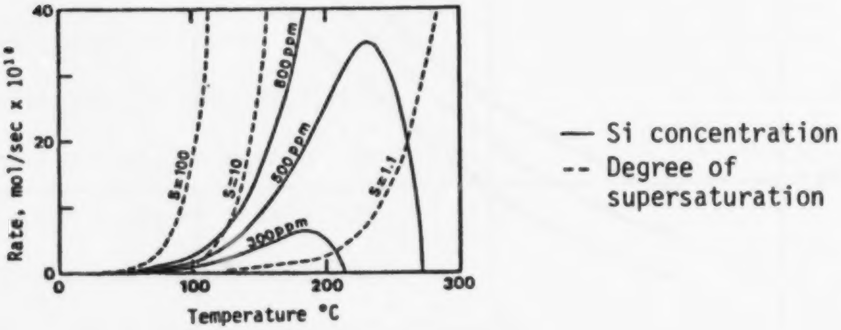
M_i = molal concentration of the i^{th} ion

V_i = valence of the i^{th} ion

These values are calculated using the chemical data already obtained. The value for the calculated solubility product K'_{sp} is then compared to the actual solubility product corrected for ionic strength (for correction technique see Appendix A). If the value calculated is larger, the chemical compound may precipitate. Alternatively solubility-ionic strength diagrams can be used. Values plotting above the solutility lines indicate thermodynamically unstable conditions where precipitation may occur. An example of such a diagram for barium sulfate is shown in Figure 14.



a. Quartz and Amorphous Silica Solubility as a Function of Temperature



b. Rate of SiO_2 Precipitation

Figure 13. Diagrams to determine silica scaling tendency (a. After Ellis and Mahon, 1977; b. After Rimstidt and Barnes, 1978).

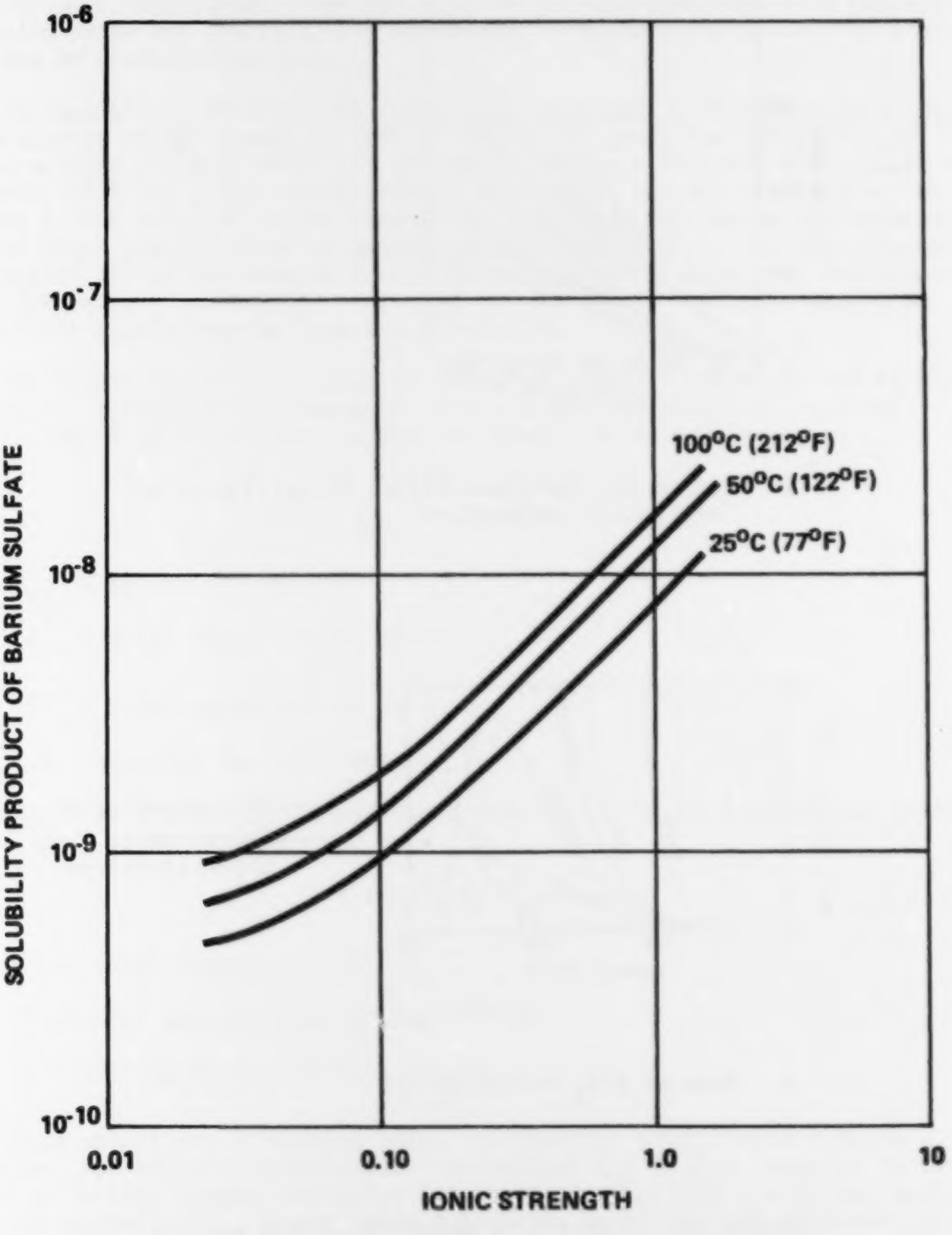


Figure 14. Solubility product versus ionic strength for barium sulfate (Bechtel, 1976).

Using these types of calculations and diagrams, chemical species which may precipitate can be identified. Table 23 compares the precipitates expected with scales found at similar geothermal sites. Selected diagrams, constants, and references are included in Appendix A.

Corrosive conditions may occur in the pipe sections where low pH, high hydrogen sulfide levels, oxygen leaks, and high fluid (erosive) velocities occur. One can predict which pipe sections will be subjected to rapid corrosion using the rates given in Table 16. This table lists corrosion rates for several pipe materials carrying geothermal fluid (steam or condensate) under low and high velocity conditions. The corrosion-erosion rates range from a low of 0.0008 mm/yr for 18-8 stainless steel pipe with fluid moving at a low velocity to a high of 1.11 mm/yr for deoxidized copper pipe with aerated steam moving at a high velocity.

How Injection Pretreatment Techniques Change Fluid Chemistry

If the fluid is injected into the subsurface region, chemical analyses of the geothermal plant discharge may indicate whether plugging or corrosion of the well casing may occur. Calcite and silica have been the most commonly occurring precipitates found in geothermal production wells and pipes to date (see Table 22). Pretreatment may be used to decrease silica concentrations and remove suspended solids. Techniques which have been tried (Bechtel, 1976; Harding-Lawson, 1978; and Quong, et al., 1978) include:

- Acid addition (H_2SO_4)
- Base addition (NaOH)
- Sedimentation and coagulation
- Application of electrical potential
- Precoat pressure filtration
- Mixed media sand filtration
- Scale inhibitor to prevent $CaCO_3$ scale

Where pretreatment is used, lab test results for the given fluid and pretreatment technique may be consulted to determine the expected concentration in the injection well. If the concentrations are low and the permeability of the formation is high, the probability of plugging and subsequently causing a well failure are less than if concentrations were high.

GROUND WATER CONTAMINATION

The third major section of the methodology is to identify potential ground water contamination. There are two basic questions:

- Can released geothermal fluid migrate to aquifers?

TABLE 23. EXAMPLE CASES OF CHEMICAL SPECIES EXPECTED TO PRECIPITATE

Parameter	Species found in scale*		Species calculated to precipitate	
	Location	Site	"Worst case"**	"Typical case"
Al			X***	X
Ba			X	
$CaCO_3$	Δ □	Pipes	X	
Cu			X	
Fe	Δ □	Pipes & casing	X	
Mg			X	
Mn	Δ			X
Ni			X	X
Pb	Δ		X	X
Sr			X	
Zn			X	X
SiO_2	Δ □	Well casing	X	X
HS			X	X
SO_4	Δ	Pipes		

* Δ Salton Sea, □ Cerro Prieto

** Similar chemistry to locations shown

*** X means species would be expected to precipitate

- Are dilution and attenuation mechanisms adequate to prevent significant levels of contamination?

These questions will be divided into steps in the following section.

Release Pathway

Geothermal fluid may reach an aquifer by percolating downward from a surface pond or spill, leaking out of a well casing, or migrating from the injection zone. Figure 15 shows how the various flow paths can be divided into three groups. Group 1 includes infiltrating flow from the ground surface to an aquifer. Leakage from a storage pond is an example of a Group 1 continuous release. A break in a surface pipe or valve is an example of a Group 1 slug release. Group 2 represents cases where a leak occurs in either a production or injection well and discharges directly into an aquifer. Group 3 represents a release from a well or injection zone at a point remote from the aquifer.

The following steps are followed to determine how ground water contamination may occur:

- Identify release group and type.
- Determine if release zone is isolated from aquifer(s).

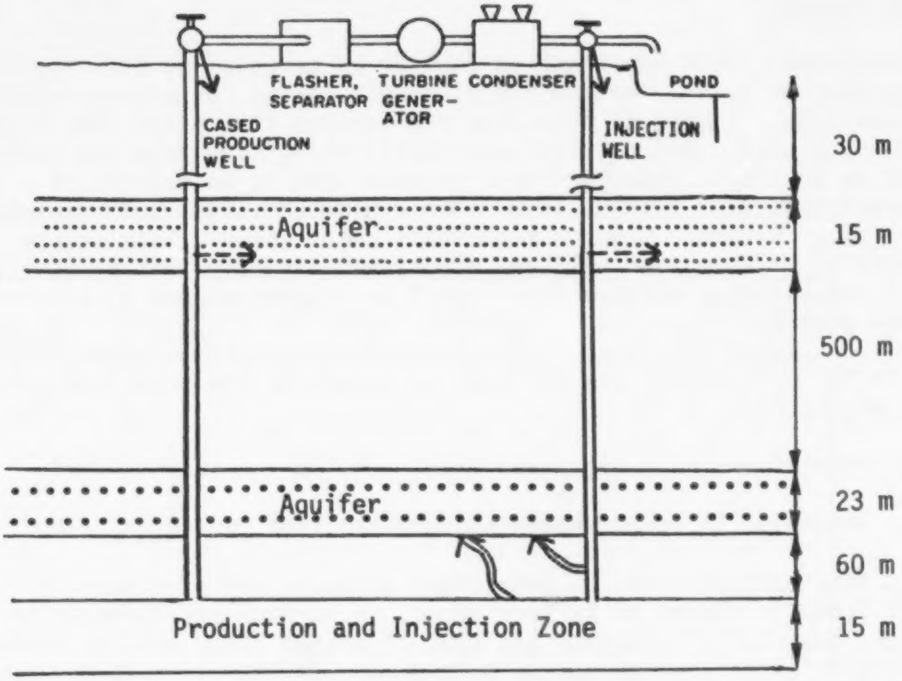
Release type and group may be determined with the aid of Figure 15. If geothermal fluid is stored in surface ponds, or surface spills would be routed to ponds, the size of the pond and type of bottom liner must be determined. The probability of leakage can be considered very low if a thick layer of clay and a liner are used and the pond has sufficient capacity to accommodate the expected flows including precipitation. Downward percolation of a release will occur in recharge areas while lateral dispersion will occur in discharge areas.

A subsurface leak from the injection zone may be isolated from usable aquifers if two conditions are met. A thick impermeable barrier (aquiclude) such as shale or massive basalt without fractured zones must be present between the injection zone and the aquifer. In addition, faults must not be present near the site. Faults may provide conduits for the movement of fluid. If these conditions are met, Group 3 type releases from the injection zone would not be considered significant. In most instances the usable aquifer will be above the injection zone but the procedure can be used for the case when the usable aquifer is below.

Extent of Potential Contamination

The procedure for determining the extent and severity of the ground water contamination includes the following steps:

- Determine if the release may be continuous or a short-term "slug" event


FLASHER, SEPARATOR
TURBINE GENERATOR
CONDENSER
POND
CASED PRODUCTION WELL
INJECTION WELL
30 m
Aquifer
15 m
500 m
Aquifer
23 m
60 m
Production and Injection Zone
15 m

NOTE: Diagram not to scale.

Key:

Release Type

⟶ Group 1

--> Group 2

⟹ Group 3

Figure 15. Hypothetical flow paths for fluid releases.

- Select appropriate solution method

- Obtain data for analyses

- Calculate resulting concentrations for aquifer of interest at zone of entry and at plant site boundary

- Determine degree of attenuation due to dilution, dispersion, and adsorption

The duration of the release determines whether it should be treated as continuous or slug flow. Continuous flow persists indefinitely and may be considered "steady-state." Frequent pulsations of slug flow over a long time period may be approximated by the steady-state case using average flow values. Slug flow is a release of a fixed length of time usually less than a year. It is applicable to the case where a leaking valve is open for a period of say 30 minutes and is then closed by an operator.

The selection of the appropriate solution method is based on the release group and time frame as shown in Table 24. The solution techniques include:

- GEOHY-GEOQAL analytical method (Gherini, 1975)

- Advection-dispersion method

- Bernoulli-Darcy approach

- Mass balance

The following sections discuss the analytical methods for each group separately giving data needs and example calculations. Attenuation mechanisms are then discussed and procedures given for determining the degree of attenuation.

Data required for all the cases include:

- Initial constituent concentrations in the released fluid

- Total mass flux (flow rate x concentration)

- Velocity of fluid movement in soil and aquifer

The first two requirements are determined in earlier steps of the procedure. The last requirement can be estimated based upon water level data at the site.

Method for Surface Releases - Group 1

Approach--

A surface release can be treated as one-dimensional flow with the pollutant moving vertically downward through the soil. This case can be

TABLE 24. SUMMARY OF SOLUTION METHODS

Release group	Release location	Time frame	Solution method
1.	Surface pond	Continuous	GEOHY-GEOQAL-A/S,* Mass balance
	Surface spill (e.g., pipeline rupture, valve failure)	Slug	Advection-Dispersion A**
	Subsurface release above Aquifer	Slug	Advection-Dispersion A
2.	Direct release into aquifer (well failure)	Continuous	Advection-Dispersion B
	Direct release into aquifer (well failure)	Slug	Advection-Dispersion A
3.	Release above or below aquifer (migration through fractures to aquifer)	Continuous	Bernoulli-Darcy Advection-Dispersion B
	Release above or below aquifer (migration through fractures to aquifer)	Slug	Bernoulli-Darcy Advection-Dispersion A

*Gherini, 1975; A/S stands for analytical solution

**Wilson and Miller, 1978; B is the modification for a continuous release. A is the modification for a slug release.

simplified by considering the velocity, moisture content, and dispersion coefficient as constant over a given depth. If the soil has several distinct layers, calculations can be performed for each layer separately. The saturated flow equation will be used to approximate flow in the unsaturated zone. The void volume will be set equal to the field capacity.

To understand how the analytical method may be used the governing equation should be briefly reviewed. The equation describing one-dimensional advective transport with dispersion and adsorption in saturated porous media is the following (Lapidus and Amundson, 1952; Gherini, 1975):

$$D \frac{\partial^2 c}{\partial z^2} - v_s \frac{\partial c}{\partial z} = \frac{\partial c}{\partial t} + \frac{1}{\varepsilon} \frac{\partial n}{\partial t} \tag{5}$$

where c = concentration of pollutant in the fluid stream, moles per liter

n = amount of pollutant adsorbed by the soil, moles per liter of soil as packed

v_s = velocity of fluid flow through interstices of the soil, m/day, approximated as $v_D/\Theta_{f.c.}$ (positive downward)

t = time, days

v_D = Darcy velocity

$\Theta_{f.c.}$ = moisture content at field capacity, decimal fraction, e.g., 0.18

z = distance down the soil, m (positive downward)

D = dispersion coefficient of the pollutant in solution in the soil, m^2/day;

ε = fractional void volume in the soil, unitless (here $\varepsilon = \Theta_{f.c.}$)

The terms in this equation from left to right represent transport due to dispersion, transport due to advection, the time rate of change in concentration of a contaminant, and last, a term which results from the consideration of adsorption of pollutants by the soil matrix.

For adsorption, the following equilibrium expression can be used to model the localized relation between c and n:

$$n = k\,c \tag{6}$$

where c and n are as defined above, and

k = an empirically determined adsorption equilibrium coefficient

Use of such an expression implies the assumption of equilibrium between the solute in solution and that adsorbed. Such an approximation approaches reality since relatively low flow velocities are encountered here. Adsorption and other attenuation mechanisms will be discussed in more detail later.

For the initial and boundary conditions stated below (i.e., initial concentration of pollutant adsorbed on the soil equals zero, initial concentration of pollutant in the soil-water solution equals zero, and the concentration of pollutant entering the soil equals a constant),

$$c\,(z,t) = 0 \quad \text{for} \quad z \geq 0 \text{ and } t = 0$$

$$n\,(z,t) = 0 \quad \text{for} \quad z \geq 0 \text{ and } t = 0$$

$$c\,(z,t) = c_o \quad \text{for} \quad t > 0 \text{ and } z = 0$$

where $c\,(z,t)$ = concentration of pollutant in the soil-water solution, at a distance z and time t, moles/liter

$n\,(z,t)$ = amount of the pollutant adsorbed, at distance z and time t, moles per liter of soil as packed

The solution of equation (5) where n is defined by equation (6) is:

$$\frac{c(z,t)}{c_o} = \frac{1}{2}\left[1 + \text{erf}\left(\frac{R - \gamma}{\sqrt{4R\gamma S}}\right) + e^{1/S}\ \text{erfc}\left(\frac{R + \gamma}{\sqrt{4R\gamma S}}\right)\right] \tag{7}$$

where c_o = pollutant concentration at z = 0

γ = $1 + \frac{k}{\varepsilon}$, a dimensionless adsorption factor

R = $\frac{v_s t}{z}$, a dimensionless time variable

S = $\frac{D_z}{z v_s}$, a dimensionless mixing factor

D_z = dispersion coefficient of the adsorbate in solution in the soil, m^2/day

z = distance down the soil, m

$\mathrm{erf}(\phi)$ = the error function of $\phi = \frac{2}{\pi} \int_0^{\phi} e^{-z^2}\, dz$

$\mathrm{erfc}(\phi) = 1 - \mathrm{erf}(\phi)$

(values for the last two functions are tabulated in Appendix D - Table D-1)

When dispersion is small relative to velocity (i.e., $S < 0.1$) the last term in equation (7) becomes negligible. This situation is typical for the conditions in which this approach will be used. Equation (7) then becomes

$$\frac{c(z,t)}{c_o} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{R - \Upsilon}{\sqrt{4R\Upsilon S}}\right)\right] \tag{8}$$

The time required for the pollutant concentration ratio $\frac{c}{c_o}$ to become equal to ½ at a given depth z, is called the "$t_{1/2}$ breakthrough time" for the propagating concentration wavefront. Inspection of equation (8) shows that this occurs when $R = \Upsilon$, or (by substitution) when:

$$t_{1/2} = \frac{z\Upsilon}{v_s} = \frac{z}{v_s}\left(1 + \frac{k}{\varepsilon}\right), \tag{9}$$

where $t_{1/2}$ = time for localized concentration (at z) to approach one-half the value of the source concentration, c_o, days

z = distance down the soil, m

v_s = velocity of fluid flow through the interstices of the soil, m/day

k = adsorption equilibrium constant (as defined by Eq. (6))

ε = fractional void volume in soil, dimensionless ($\varepsilon = \frac{p}{1-p}$ where p is porosity)

The solution for the "breakthrough times" associated with other than the $\frac{c}{c_o} = 0.5$ ratio can be readily evaluated (Gherini, 1975). It can be shown that the error function (erf) is related to the probability integral, such that

$$\mathrm{erf}(\Theta) = 2\phi\left(\sqrt{2}\ \Theta\right) \tag{10}$$

where the probability integral $\phi(\Theta) = \frac{1}{\sqrt{2\pi}} \int_{o}^{t'} e^{-\frac{w^2}{2}} dw$

By substitution into Eq. (8),

$$\frac{c}{c_o} = \frac{1}{2} + \int_{o}^{\left(\frac{R - \Upsilon}{\sqrt{2R\Upsilon S}}\right)} \phi(u)\, du \qquad (11)$$

where $\phi(u) = \frac{1}{\sqrt{2\pi}} e^{-\frac{w^2}{2}}$

Other terms are as defined for Eq. (6).

The values of the probability integral are presented in Table D-2 in Appendix D. One enters the table with "area" equal to $\frac{c}{c_o} - \frac{1}{2}$ and reads the value of t', (the so-called standard unit). This value is equated to the upper limit of the integral in Eq. (12) resulting in a quadratic equation:

$$t' = \left(\frac{R - \Upsilon}{\sqrt{2R\Upsilon S}}\right) \quad , \quad R^2 - \left[2\Upsilon + 2\Upsilon S(t')^2\right] R + \Upsilon^2 = 0 \qquad (12)$$

The two roots can then be solved for the related "breakthrough times." The larger root is associated with the higher $\frac{c}{c_o}$ ratio, such as $\frac{c}{c_o} = 0.90$, and the smaller root with the smaller complementary ratio, $\frac{c}{c_o} = 0.10$. The $\frac{c}{c_o} = 0.9$ breakthrough time is computed as follows:

$$\int_{o}^{\left(\frac{R - \Upsilon}{\sqrt{2R\Upsilon S}}\right)} \psi\,(u)\, du = \left| \frac{c}{c_o} - 0.5 \right| = |0.9 - 0.5| = 0.4 = \text{"Area"}$$

Entering the probability integral table with area = 0.4, a t' value of 1.28 is read (area = 0.3997 → t = 1.28). t = 1.28 is substituted into Eq. (12) and the roots R are computed. A simplified form for the solution of Eq. (12) for the two roots is the following:

$$R = \Upsilon m \left[1 \pm \sqrt{1 - \frac{1}{m^2}} \right]$$

where $m = \left(1 + St'^2 \right)$

and as before,

$s = \frac{D}{zv_s}$, the dimensionless mixing factor

$\Upsilon = 1 + \frac{k}{\varepsilon}$, the retardation constant

t'= the "standard unit" from the probability tables for $\left| \frac{c}{c_o} - \frac{1}{2} \right|$ taken as the "area"

Given the roots R_1 and R_2 the breakthrough times are calculated as $t_{90} = \frac{R_1 z}{v_s}$ $t_{10} = \frac{R_2 z}{v_s}$

Analytical Procedure--

Equation (8) may be used to calculate pollutant concentrations at a specific depth below the surface. This equation is referred to in this report as the GEOHY-GEOQAL Analytical Solution. The steps involved in the calculations are:

- Compile site specific data
- Calculate the dimensionless adsorption factor, Υ
- Estimate the dispersion coefficient, D_z
- Calculate the dimensionless time variable, R
- Calculate the mixing factor, S (use Eq. (8) only if $S < 0.1$)
- Substitute values into equation (7) or (8) for various combinations of z and t

Data needed include:

- $\Theta_{f.c.}$ = soil moisture content at field capacity (to be used as an estimate of the void volume ε)
- k = adsorption coefficient for each pollutant, for conservative pollutants, e.g., Cl^-, assume $k = 0$.

- v_s = seepage velocity, m/day ($V_D/\Theta_{f.c.}$)
- D_z = dispersion coefficient of the pollutant in the soil-water solution, m^2/day
- z = distance down soil, m (positive downward)
- c_0 = initial concentration of pollutant in the solution entering the soil, e.g., mg/ℓ

The soil moisture content at field capacity can be measured by commercial laboratories or can be estimated based on soil composition using Table B-3 in Appendix B. If site-specific adsorption coefficients have not been measured by field or lab tests, approximate values may be selected from those given in Appendix C or from values given in chemical literature. Laboratory conditions may not be similar to those at the site and soil ion concentrations may not be well known. Obtaining adsorption values may be difficult.

Seepage velocities can be obtained from field measurements, detailed calculations based on permeability, k(Θ), and potential, Ψ(Θ), relationships or water balance calculations (e.g., Fenn, Hanley, and De Geare, 1975). Compatible particle sizes and seepage velocities may be chosen from the table in Appendix B (Table B-1) if site-specific data are limited.

The dispersion coefficient is difficult to measure independently at the site. It can be estimated by the following procedure:

- Calculate the Peclet number, P_e
- Use Figure 16 to estimate the ratio of dispersion to molecular diffusion, D_L'/D_d
- Multiply the above ratio by D_d to obtain D_L'

The Peclet number (P_e) is defined as follows:

$$P_e = \frac{V_s g}{D_d} \tag{13}$$

where g = the mean soil grain size, m;

D_d = molecular diffusion coefficient, $\frac{m^2}{day}$

V_s = seepage velocity $\simeq \frac{V_{Darcy}}{\Theta}$, $\frac{m}{day}$ where

Θ = volumetric moisture fraction, dimensionless

Values for the ratio of longitudinal dispersion to molecular diffusion D_L'/D_d can be obtained graphically using Figure 16. One obtains longitudinal dispersion by multiplying this ratio by the molecular diffusion constant. For

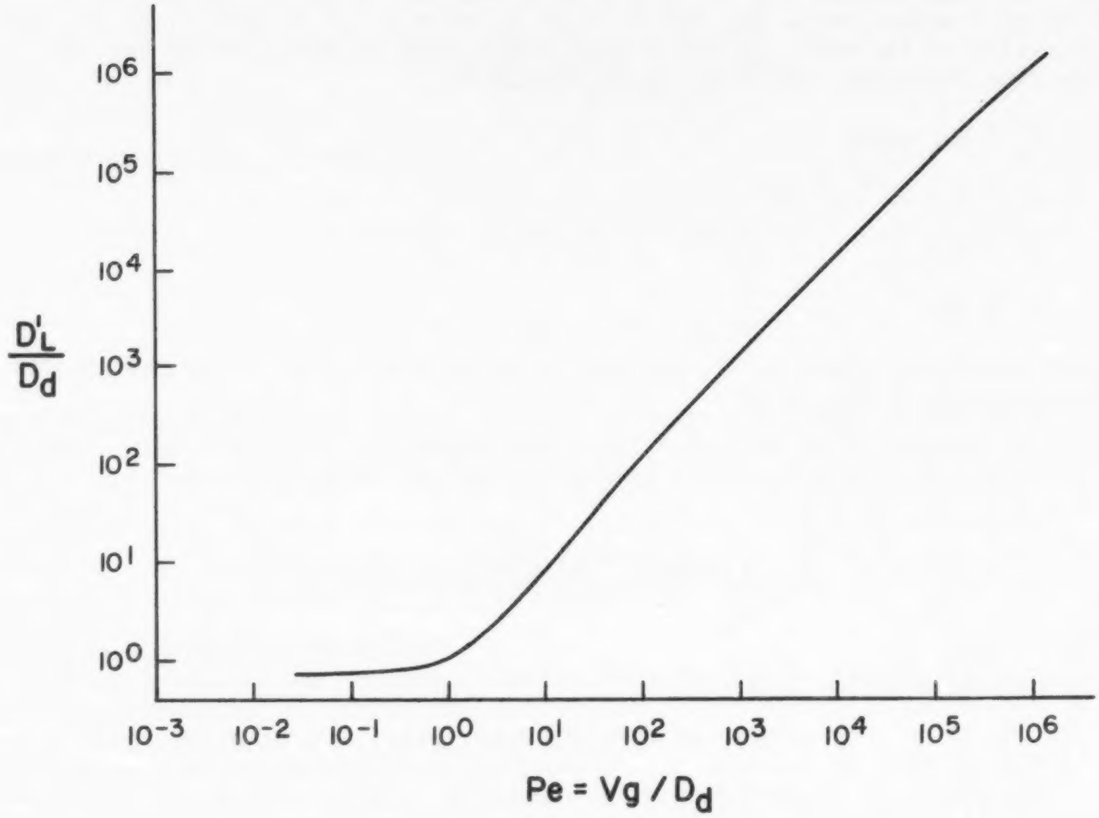


Figure 16. Graph of relationship of Peclet number to convective dispersion (after Bear, 1975).

aqueous contaminants the value of this constant at 20°C is approximately 10^{-4} m^2/day. The value of the transverse dispersion coefficient, D_Z, typically ranges from 0.1 to 0.7 times the longitudinal dispersion coefficient.

Example Problem 1 - "Breakthrough Times"

Aqueous mercury is leaking from a large unlined storage pond. Determine the time required for the concentration of mercury in soil solution, at a depth of 3 meters below the pond bottom, to reach 5 and 95 percent of the concentration in the pond. The following values have been determined for the site from field and laboratory measurements:

$V_s \cong 0.1$ m/day

$D \cong 8 \times 10^{-5}$ m^2/day

$\varepsilon \cong 0.4$

$K \cong 400$

First calculate values for γ, the dimensionless adsorption factor, and S, the dimensionless mixing factor:

$$\gamma = \left(1 + \frac{k}{\varepsilon}\right) = \left(1 + \frac{400}{0.4}\right) = 1001$$

$$S = \frac{D}{V_s z} = \frac{8\text{x}10^{-5}\ m^2/\text{day}}{0.1\ \text{m/day x 3m}} = 2.67\text{x}10^{-4}$$

Next calculate t' for c/co = 0.95

$$t' = |0.95 - \tfrac{1}{2}| = 0.45$$

The area read from Table D-2 in Appendix D is 1.64.

Now the roots of Eq. (12) are evaluated

$$m = 1 + \left[2.67\text{x}10^{-4} \text{ x } (1.64)^2\right]$$

$$= 1.00072$$

$$R = 1001\ (1.00072)\ \left[1 \pm \sqrt{1 - \frac{1}{(1.00072)^2}}\right]$$

$$= 1040,\ 963$$

Finally, time required for the concentration of pollutant at 3 meters to reach 95 percent of the influx pollutant concentration c_o is calculated:

$$t = \frac{Rz}{v_s} = \frac{1040 \times 3 \text{ m}}{0.1 \text{ m/day}} = 3.12 \times 10^4 \text{ days}$$
$$= 85.5 \text{ years}$$

To reach 5 percent of the influx pollutant concentration

$$t = \frac{Rz}{v_s} = \frac{963 \times 3 \text{ m}}{0.1 \text{ m/day}} = 2.89 \times 10^4 \text{ days}$$
$$= 79.1 \text{ years}$$

Summarizing the example case,

$$t \text{ (for } \frac{c}{c_o} = .95) = 85.5 \text{ years}$$

$$t \text{ (for } \frac{c}{c_o} = .05) = 79.1 \text{ years}$$

The resulting breakthrough wave of mercury is quite steep and considerably delayed. Water molecules and constituents which are not soil interactive (k=0) would, on the average, tranverse the same distance in only 30 days.

$$\frac{z}{v_s} = \frac{3 \text{ m}}{0.1 \text{ m/day}} = 30 \text{ days}$$

Resulting Aquifer Concentration--

After computing the concentration reaching the top of the aquifer, the resulting concentration within the aquifer can be calculated in two ways: by use of simple mass balance expressions assuming no attenuation, or by use of advection-dispersion equations with allowance for attenuation (see for example, Wilson and Miller, 1978). The mass balance approach is discussed in this section. The advection-dispersion method allowing attenuation is discussed under Group 2 calculations.

The mass balance approach computes the concentration in the aquifer using the following equation:

$$c = \frac{Q_p c_p + Q_A c_A}{Q_p + Q_A} \tag{14}$$

where c = resulting concentration in aquifer

Q_p = volumetric flow rate of liquid transporting pollutant into aquifer ($Q_p = V_{D_z} A_p$)

V_{D_z} = Darcy velocity in the downward direction ($V_{D_z} \cong V_s\varepsilon$)

A_p = horizontal area of pond or spill

c_p = concentration of pollutant at upper boundary of the aquifer (unsaturated-saturated zone interface)

Q_A = volumetric flow rate of aquifer ($Q_A = V_D hw$)

V_D = Darcy velocity in aquifer

h = thickness of aquifer

w = surface pond or spill width perpendicular to flow direction in aquifer

c_A = initial concentration of pollutant in aquifer

This approach assumes complete mixing with that portion of the aquifer directly under the pollutant source.

Example Problem 2 - "Resulting Aquifer Concentrations"

The leaking storage pond in Example Problem 1 also contains a high concentration (1000 mg/l) of chloride ion, a pollutant which is not absorbed by soil. The pond has a surface area of 1200 m^2. The width of the pond normal to the aquifer flow direction is 50 meters. The thickness of the unconfined aquifer is 15 meters and velocity of fluid movement in the aquifer is estimated to be 0.08 m/day. Assume the background concentration of chloride in the aquifer is 20 mg/ℓ. Make an estimate of the likely resulting chloride concentration in the aquifer.

Recall from Sample Problem 1

V_s = 0.1 m/day

ε = 0.4

First calculate Q_p and Q_A

$$Q_p = V_{D_2} A_p$$

$$V_{D_2} = V_s\ \varepsilon = 0.1 \text{ m/day} \times 0.4 = 0.04 \text{ m/day}$$

$$Q_p = 0.04 \text{ m/day} \times 1200 \text{ m}^2 = 48 \text{ m}^3\text{/day}$$

$$Q_A = V_D hw = 0.08 \text{ m/day} \times 15 \text{ m} \times 50 \text{ m} = 60 \text{ m}^3\text{/day}$$

substituting into equation (14):

$$c = \frac{48\ \text{m}^3/\text{day} \times 1000\ \text{mg}/\ell + 60\ \text{m}^3/\text{day} \times 20\ \text{mg}/\ell}{48\ \text{m}^3/\text{day} + 60\ \text{m}^3/\text{day}}$$

$$c = 456\ \text{mg}/\ell$$

Concentrations resulting from a slug release at the surface can be estimated using the advection-dispersion method case A as described for Group 2 releases.

Method for Direct Releases into Aquifers from Wells-Group 2

Approach--

Direct releases into an aquifer may occur from an injection or production well due to casing leaks, cement failure, or migration along the wellbore. The pollutant concentration may attenuate by dispersion, dilution, and adsorption within the aquifer. If the aquifer can be considered to be vertically mixed, the advection-dispersion method can be used to obtain the resulting downstream concentrations in the aquifer.

This method is based on the following differential equation which describes mass transport in uniform steady flow in the x direction, with dispersion and adsorption. The derivation of the equation is presented by Bear (1975). A solution is given by Wilson and Miller (1978), and by Codell (1978).

$$R_d \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - V_x \frac{\partial c}{\partial x} - \lambda R_c c \qquad (15)$$

where c = concentration of pollutant in solution

t = time

R_d = the retardation factor, $1 + \frac{k}{\varepsilon}$, (same as γ in Eq. (7))

λ = first order solute decay constant (change in tracer concentration resulting from this decay alone is expressed $\frac{\partial c}{\partial t} = -\lambda c$)

D_z = longitudinal dispersion coefficient

D_y, D_x = transverse dispersion coefficients

Redefining the variables in terms of R_d yields

$$\frac{\partial c}{\partial t} + V' \frac{\partial c}{\partial x} = D'_x \frac{\partial^2 c}{\partial x^2} + D'_y \frac{\partial^2 c}{\partial y^2} + D'_z \frac{\partial^2 c}{\partial z^2} - \lambda c \qquad (16)$$

For a slug release, case A, with an instantaneous injection along the x axis, Eq. (16) after integrating in two dimensions yields (Wilson and Miller, 1978, Codell, 1978)

$$c(x,y,t) = \frac{1}{R_d} \frac{m'}{4\pi p t (D_x D_y)^{\frac{1}{2}}} \exp \left[- \frac{(x - V_s t)^2}{4D_x t} - \frac{y^2}{4D_y t} - \lambda t \right] \qquad (17)$$

where m' = total mass of solute injected into the aquifer per unit thickness of aquifer (d) along the vertical z axis, e.g., mg/ft

p = effective porosity

D_x = dispersion in x direction, m^2/day

D_y = dispersion in y direction, m^2/day

x,y = distance from source (flow parallel to x axis), m

V_s = seepage velocity, m/day

t = time, days

R_d = retardation factor

Solution Procedure--

The advection-dispersion equation case A may be solved by substitution (Example Problem 3) or by a graphical technique which will be explained in the section on Group 3.

Example Problem 3 - "Aquifer Concentration Following Slug Injection"

Calculate the pollutant concentration at the surface of an aquifer 300 m downstream from a slug release 700 days after it occurred. The release flows directly into an aquifer with a thickness of 9 meters and is assumed to distribute itself instantaneously in the vertical direction (within the aquifer). The pollutant decay rate is 3.4×10^{-3} day^{-1}. The seepage velocity in the aquifer is 0.48 m/day in the horizontal direction. The total pollutant mass of the slug release is 1.8×10^8 mg. Other input data are given below:

$d = 9$ m

$$m' = \frac{1.8 \times 10^8 \text{ mg}}{9 \text{ m}} = \frac{2 \times 10^7 \text{ mg}}{\text{m}}$$

$p = .35$

$D_x = .93\ m^2/day$

$D_y = .56\ m^2/day$

$R_d = 1$ if $k = 0$

Use Eq. (17):

$$C = \frac{1}{R_d} \frac{m'}{4\pi pt(D_x D_y)^{\frac{1}{2}}} \exp\left[-\frac{(X-V_s t)^2}{4D_x t} - \lambda t\right]$$

Substituting into Eq. (17) gives:

$$C = \frac{1}{1} \frac{2 \times 10^7}{4\pi(.35)\ 700\ (.93 \times .56)^{\frac{1}{2}}} \exp\left[-\frac{(300-(.48 \times 700))^2}{4 \times .93 \times 700} - 3.4 \times 10^{-3}\ (700)\right]$$

$$C = \frac{2 \times 10^7}{2.22 \times 10^3} \exp[-2.87] = 510.8\ mg/m^3 = 0.51\ mg/\ell$$

The time to reach the maximum value of solute concentration ($c^{\dagger}$) in the aquifer may be calculated by determining the derivative $\frac{dc}{dt}$ of Eq. (17) and setting this equal to zero. This has been done by Hunt (1978). The results are presented by the following equation:

$$t_{max} = \frac{\left(\sqrt{1 + \left(\frac{V_s r'}{nD_x}\right)^2} - 1\right) n\ D_x}{{V_s}^2} \qquad (18)$$

where t_{max} = time to reach maximum concentration

V_s = seepage velocity, m/day

r' = for 1 dimension = x_1 $(x>0)$

for 2 dimensions = $\sqrt{x^2+y^2(D_x/D_y)}$

for 3 dimensions = $\sqrt{x^2+y^2(D_x/D_y) + z^2(D_x/D_z)}$

n = number of dimensions (e.g., 1, 2, or 3)

D_x = dispersion redefined here as ≈ D_x/R_d

R_d = retardation factor

The steps for determining the maximum concentrations are:

- Use data obtained for Eq. (17)
- Calculate time to reach maximum concentration using Eq. (18)
- Substitute the time to reach maximum into Eq. (17)
- Calculate the maximum concentration.

Example Problem 4 - "Maximum Concentration in Aquifer"

Determine the maximum concentration and the time of occurrence resulting from the break described in Example Problem 3 at a distance of 300 meters in the direction of flow.

Input data from Example Problem 3.

Use Eq. (18):

$$t_{max} = \frac{\left(\sqrt{1 + \left(\frac{V_s r'}{nD_x}\right)^2} - 1\right) n\ D_x}{V_s^2}$$

Substituting the data into Eq. (18) gives:

$$t_{max} = \frac{\left[\left[1 + \left(\frac{.48\ m/day \times 300\ m}{2 \times .93\ m^2/day}\right)^2\right]^{1/2} - 1\right] 2\ (.93\ m^2/day)}{(.48\ m/day)^2}$$

$$= 617\ days$$

Substituting t_{max} into Eq. (17) gives

$$c_{max} = \frac{1}{1} \frac{2 \times 10^7}{4\pi\ (.35)(617)(.93 \times .56)^{1/2}} \exp\left[- \frac{(300\ m - .48\ m/day\ (617\ days))^2}{4\ (.93\ m^2/day)\ 617} - \frac{(0)^2}{4\ (.56)\ 617} - 3.4 \times 10^3\ 617\right]$$

$$\varsigma_{max} = \frac{2 \times 10^7}{1.96 \times 10^3} \exp \left[- .006 - 2.10 \right] = 1242 \text{ mg/m}^3$$

$$= 1.24 \text{ mg/}\ell$$

The concentrations in an aquifer resulting from a direct release from a continuous source can be estimated using the advection-dispersion method, case B. Eq. (16) is solved for the steady-state case. The procedure and an example problem are described in the section on Method for Releases at Depth - Group 3.

Method for Releases at Depth - Group 3

Approach--

Releases above or below the aquifer of concern could migrate to the aquifer. Several approaches to flow in porous, fractured media were considered (Witherspoon, 1975; Lippman, 1977; Horne and Ramey, 1978). A feasible approach which does not require extensive data or calculations is to simply use Bernoulli's equation for flow through pipes to calculate the pressure at the location of the break in the well and Darcy's law to calculate the flow into an aquifer. If data are available on permeability and area of the fracture zone, then this approach is the most direct.

When such data are not available, then a conservative approach could be taken stating that the flow rate into the aquifer is the same as at the failure location. The worst case would be a complete severing of the well and loss of the total well flow rate to the aquifer. For casing leaks, only a percentage of the well flow may be lost and/or enter the aquifer.

Figure 17 shows an example cross section with a hypothetical well rupture. Well size and flow rate are obtained for the site.

The Bernoulli equation can be used for calculating the pressure at the point of rupture, P_2 (shown in Figure 17), as follows:

$$\frac{P_2}{\gamma} = \frac{P_1}{\gamma} + L + f \frac{L}{D} \frac{V_1^2}{2g} \tag{19}$$

where P_2 = pressure at failure location

P_1 = pressure at wellhead

V_1 = velocity in well ($V_1 = Q/A$), m/sec

Q = well flow rate, m^3/sec

A = cross-sectional area of well, m^2

g = 9.76 m/sec^2 (gravitational acceleration constant)

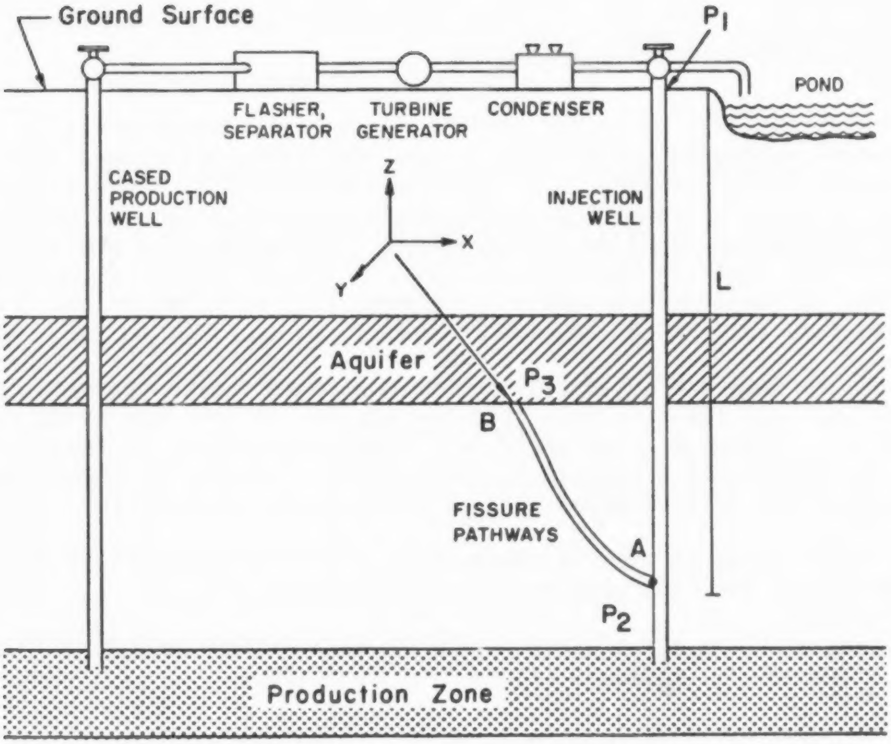

Ground Surface
P1
POND
FLASHER, SEPARATOR
TURBINE GENERATOR
CONDENSER
CASED PRODUCTION WELL
Z
X
Y
INJECTION WELL
L
Aquifer
P3
B
FISSURE PATHWAYS
A
P2
Production Zone

Figure 17. Schematic diagram for group 3 case.

γ = specific weight of liquid

f = friction factor

L = length of well down to failure location, m

D = diameter of well, m

The friction factor (f, here a constant), for the well casing can be estimated from the roughness of the pipe, pipe diameter, and the Reynolds number using a form of the Moody diagram. Appendix E (Figure E-2) gives relative roughness values for different diameters and types of pipes. The following equation is used to calculate Reynolds number:

$$N_R = \frac{DV}{\nu} \tag{20}$$

where N_R = Reynolds number

D = pipe diameter, m

V = velocity, m/s

ν = kinematic viscosity of liquid, m^2/sec (values given in Appendix E - Table E-1)

The friction factor is read from the Moody diagram (in Appendix E - Figure E-1) based on the relative roughness and Reynolds number. Typically an iterative solution must be made since "f" depends upon the velocity of flow in the pipe.

Analytical Procedure--

The steps for the "Bernoulli-Darcy" approach are as follows:

- Obtain data needed
- Estimate friction factor
- Calculate pressure at failure location
- Calculate flow into aquifer using Darcy's law
- Calculate concentration in aquifer using mass balance approach or advection-dispersion method

Data needed are:

- Depth of well to failure location
- Diameter of well
- Well flow rate

- Area of well cross section
- Friction factor
- Location of aquifer

Example Problem 5 - "Pressure at the Point of Rupture"

Determine the well pressure at a rupture occurring 250 meters below the surface given the following information. Assume the friction factor has a constant value of 0.019.

Values refer to Figure 17.

P_1 = 24.6 Kg/cm^2

L = 250 m

f = 0.019

D = .3 m

V_1 = .43 m/sec

ratio of $\gamma_{\text{geothermal fluid}}/\gamma_{\text{water}}$ = 1.19

γ_{water} = 999.4 Kg/m^3

Use Eq. (19):

$$\frac{P_2}{\gamma} = \frac{P_1}{\gamma} + L + f\,\frac{L}{D}\;\frac{V_1}{2g}^{\,2}$$

Substituting the data gives

$$\frac{P_2}{\gamma} = \frac{24.6 \times 10{,}000}{999.4 \times 1.19} + 250 + 0.019\,\frac{(250)}{.3}\;\frac{.185}{2 \times 9.76}$$

$$= 206.8 + 250 + .15 = 457 \text{ m}$$

$$P_2 = 457 \text{ m} \times (1.19)\ (999.4 \text{ Kg/m}^3)\ (1 \text{ m}^2/10{,}000 \text{ cm}^2$$

$$= 54.35 \text{ Kg/cm}^2$$

For the case of a fractured aquifer the following form of Darcy's law may be used to approximate the flow, Q_3, through a fracture zone to the aquifer:

$$Q_3 = KA\left(\frac{\frac{P_2 - P_3}{\gamma}}{(L-B)}\right) \qquad (21)$$

where Q_3 = flow rate into the aquifer

K = permeability of fracture zone

A = cross sectional area of fracture zone

P_3 = pressure in the aquifer at geothermal entry point, $P_3 = h\gamma$

h = depth of water in the aquifer, if unconfined aquifer

= hydrostatic head of water, if confined aquifer

γ = specific weight of geothermal fluid

$(L-B)$ = approximation to length of fracture zone flow path (see Figure 17 - B is depth to base of aquifer

Note: The flow is considered to be laminar in this equation so N_R' must be less than or equal to 10.

$N_R' = \frac{Vd}{\nu}$, where d is an estimate of the average particle size in the fracture zone

Example Problem 6 - "Flow at Aquifer"

Estimate the flow into the aquifer of Problem 5 resulting from the rupture of the well casing.

Input data are from Example Problem 5 and the following values.

$L-B = 56$ m

$K = 9.55$ m/day (ℓ/m^2/day)

$A = 3.14\ m^2$ if circular zone of 2 ft diameter

$\frac{P_2}{\gamma} = 457$ m

$\frac{P_3}{\gamma} = 9$ m

Use Eq. (21):

$$Q_3 = KA\left(\frac{P_2 - P_3}{\frac{\gamma}{(L-B)}}\right)$$

$$Q_3 = 9.55 \text{ m/day} \times 3.14 \text{ m}^2 \times \frac{(457 \text{ m} - 9 \text{ m})}{(56 \text{ m})}$$

$$Q_3 = 239.9 \text{ m}^3\text{/day} = 166.6 \text{ ℓpm}$$

Resulting Concentration in Aquifer--

The next step is to estimate the concentration within the aquifer using the advection-dispersion approach for a continuous release or the mass balance approach discussed under the section for Group 1 releases. For a slug case the aquifer concentration would be calculated using the advection-dispersion method case A as described under Group 2 releases. Eq. (16) (the advection-dispersion equation) can be solved for the continuous injection rate (case B) (Wilson and Miller, 1978) and yields

$$c(x,y,t) = \frac{f'_m \exp \frac{x}{B}}{4\pi p(D_x D_y)^{\frac{1}{2}}} W\left(u, \frac{r}{B}\right) \tag{22}$$

where c = concentration in the aquifer, e.g., mg/ℓ

f'_m = mass flux injection rate, injected uniformly over the aquifer thickness = qc_o, e.g., mg/m/day

q = volumetric injection rate per unit length, e.g., m^3/m day

c_o = initial concentration of pollutant (at source), e.g., mg/ℓ

p = porosity, decimal fraction

$W(u,\frac{r}{B})$ = well function

u = $r^2/4\gamma' D_x t$, e.g., m/day

B = $2D_x/V_s$, unitless

r = function of radial distance from source, m =

$$\left[\left(x^2 + \frac{D_x}{D_y} y^2\right) \gamma'\right]^{\frac{1}{2}}$$

γ' = $1 + \left(\frac{2B\lambda}{V_s}\right)$ if no solute decay $u = \frac{r^2}{4D_x t}$

V_s = seepage velocity, m/day

The procedure is as follows:

- Obtain data
- Calculate dispersion constant if not measured
- Evaluate the well function
- Substitute data into Eq. (22)
- Calculate resulting concentrations in the aquifer at points and times of interest

The mass flux, initial pollutant concentration, and injection rate can be estimated based on data in the section on chemistry of spilled fluid. Procedures for obtaining the dispersion constant were discussed in the section on Methods for Surface Releases--Group 1. The well function for r/B ratios <10 is available from plots and tables (DeWiest, 1967). For larger r/B ratios the following approximation can be used (Wilson and Miller, 1978):

$$W(u,\ r/b) \simeq \left(\frac{\pi B}{2r}\right)^{\frac{1}{2}} \exp\ (-r/B)\ \mathrm{erfc}\ \ -\left(\frac{(r/B)\ -\ 2U}{2(u)^{\frac{1}{2}}}\right) \tag{23}$$

Appendix D includes a tabulation (Table D-1) of the complementary error function (erfc) and the error function (erf). For a steady-state case a modified Bessel function (K_0 (r/B)) as given below may be substituted for the well function for cases with $r/B > 1$, as is typically the case here.

$$K_0\ (r/b) \simeq \left(\frac{2r}{\pi B}\right)^{-\frac{1}{2}} \exp -r/B \tag{24}$$

Eq. (22) may be solved by direct substitution. This is satisfactory if only a small number of solutions are needed. If many solutions are desired, then a graphical solution technique may be used.

Example Problem 7 - "Aquifer Concentrations"

Estimate the concentration increase after 667 days of a conservative pollutant 300 m down-flow from the line of contamination in the example aquifer resulting from a continuous release. Additional input data are summarized below. The waste flows into the aquifer at about 3.78 ℓpm with a concentration of 200 mg/ℓ.

p = .35

t = 667 days

D_x = .93 m^2/day

D_y = .56 m^2/day

x = 300 m

y = 0 m

d = 9.15 m

V_s = .46 m/day

λ = 3.4×10^{-3} day^{-1}

Evaluate the well function:

$$r = \left[x^2 + \frac{D_x}{D_y} y^2 \gamma\right]^{\frac{1}{2}} = \left[\left(300\right)^2 + \frac{.93}{.56} (0)^2 \; 1.06\right]^{\frac{1}{2}} = 300 \text{ m}$$

$$B = \frac{2D_x}{V_s} = \frac{2(.93 \text{ m}^2/\text{day})}{.46 \text{ m/day}} = 4.04 \text{ m}$$

$$\gamma = 1 + \frac{2B\lambda}{V_s} = 1 + \frac{2(4.04)(3.4 \times 10^{-3})}{.46} = 1.06$$

$$u = r^2/4\gamma D_x t$$

$$u = \frac{(300 \text{ m})^2}{4(1)(.93 \text{ m}^2/\text{day})(667 \text{ days})} = 36.27$$

Substitute these values into Eq. (23)

$$W(u,r/B) = \left(\frac{\pi 4.04}{2\text{x}300}\right)^{\frac{1}{2}} \; \exp \left(\frac{300}{4.04}\right) \; \text{erfc} - \frac{\frac{300}{4.04} - 2\;(36.3)}{2(36.3)^{\frac{1}{2}}}$$

$$= (0.145) \; \exp\left(-\frac{300}{4.04}\right) \; \text{erfc}\left(-\;12.19\right)$$

$$= (0.145) \; \exp\left(-\frac{300}{4.04}\right)\left[1 - (-1) \; \text{erf}\left(12.19\right)\right]$$

$$= (0.145) \; \exp\left(-\frac{300}{4.04}\right) \; (1)$$

Use Eq. (22):

$$C(x,y,t) = \frac{f'_m \exp \frac{x}{B} W(u,r/B)}{4\pi p(D_x D_y)^{\frac{1}{2}}}$$

$$f'_m = \frac{5.45 \times 10^3 \times 200}{9.15} = 1.19 \times 10^5 \text{ mg/m/day}$$

Substitute the above data into Eq. (22)

$$C = \frac{1.19 \times 10^5 \text{ mg/m/day} \exp \frac{300 \text{ m}}{4.04 \text{ m}}}{4\pi \; (.35)(.93 \text{ m}^2/\text{dayx}.56 \text{ m}^2/\text{day})^{\frac{1}{2}}} W(36.3,\ 74.26)$$

$$C = \frac{5436 \text{ mg}}{\text{m}^3} = 5.4 \text{ mg}/\ell$$

To compute the steady-state concentration resulting from a continuous leak Eq. (22) may be used. The only difference in the formulation of the equation for the steady-state case and the time after release case is the substitution of the modified Bessel function for the well function. The equation then becomes

$$\overline{C} = \frac{f'_m \left[\exp \frac{x}{B}\right]\left[\left(\frac{2r}{\pi B}\right)^{-\frac{1}{2}} \exp - r/B\right]}{2\pi p \; (D_x D_y)^{\frac{1}{2}}} \qquad (25)$$

where $\overline{C}$ is the steady-state concentration.

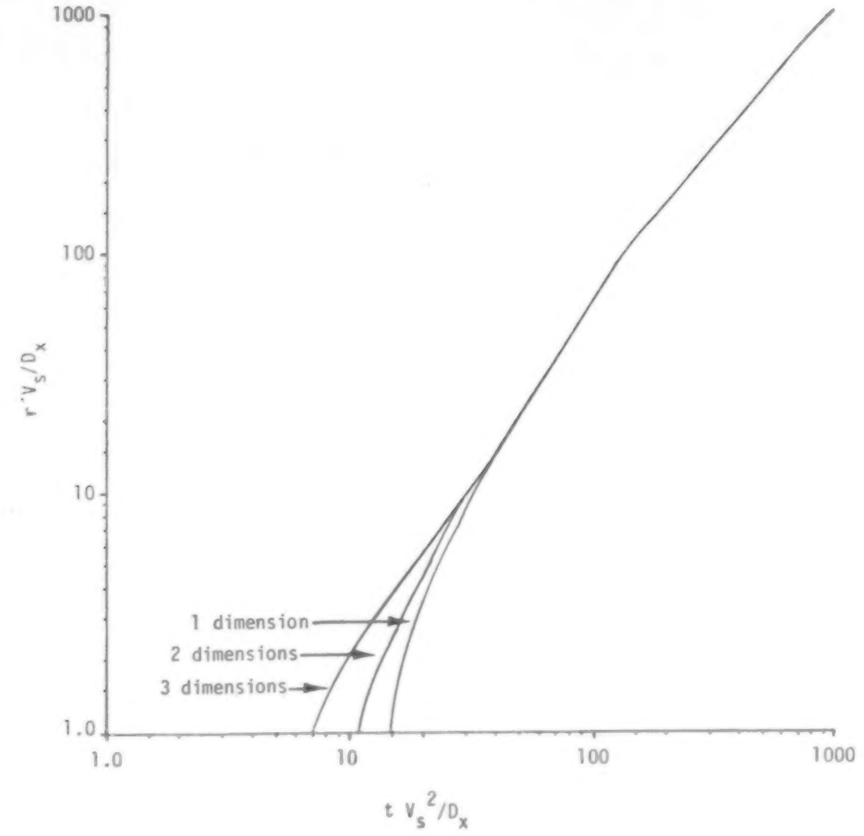
The equation is solved by substituting the appropriate data as shown below with data from Example Problem 7.

$$\overline{C} = \frac{1.19\text{x}10^5 \text{ mg/m/day} \left[\exp \frac{300 \text{ m}}{4.04 \text{ m}}\right]\left[\left(\frac{2 \cdot 300}{\pi \; 4.04}\right)\text{m}^{-\frac{1}{2}} \exp\ (-74.26)\right]}{2(\pi)(0.35)(.93 \times .56)^{\frac{1}{2}}}$$

$$= 10906 \text{ mg/m}^3 = 11 \text{ mg}/\ell$$

The time required to reach steady state can be estimated graphically using Figure 18. The value of the term $r'V_s/D_x$ (defined on Figure 18) is calculated and the corresponding value for $t\ V_s^2/D_x$ is read from the abscissa. Values are substituted for V_s and D_x and the expression solved for t, the time to reach steady state.

Alternatively, one may solve Eq. (22) graphically. The graphical solution (Wilson and Miller, 1978) involves the following steps:



Key:

Number of Dimensions	Definition of r′
One	$x\ (x > 0)$
Two	$\left(x^2 + y^2\ (D_x/D_y)\right)^{1/2}$
Three	$\left(x^2 + y^2\ (D_x/D_y) + 2^2\ (D_x/D_z)\right)^{1/2}$

Figure 18. Time for release to reach steady-state conditions (after Hunt, 1978).

- Calculate r/B values for selected x and y values
- Plot r/B curves as function of x/B and y/B
- The plotted results would look like Figure 19a if $D_x/D_y = 1$ or Figure 19b if D_x and D_y are not equal
- Pick steady state concentration of interest, $\overline{C}$
- Calculate $C^{\dagger}$ where $C^{\dagger} = \dfrac{f'_m}{p(8\pi D_x D_y)^{\frac{1}{2}}}$
- Calculate $\overline{C}/C^{\dagger}$ ratio
- Determine $\dfrac{(r - x)}{B}$ value from Figure 19c
- Plot $\overline{C}$ contours as shown on Figure 19b

How Much Will Attenuation Decrease Contamination

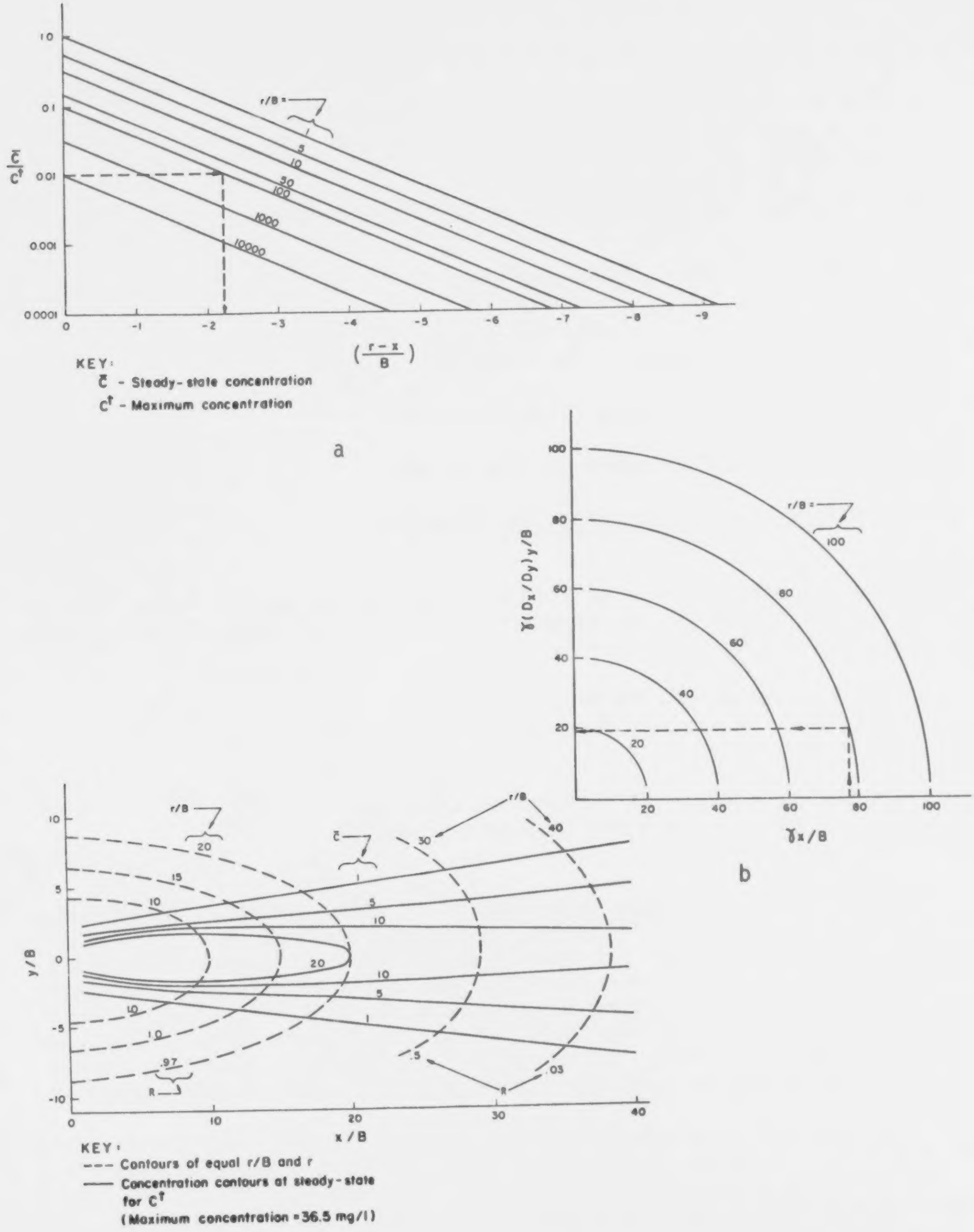
Mechanisms--

If the concentrations calculated without attenuation are higher than the appropriate use standards, the concentrations should be recalculated allowing for attenuation. The procedure is:

- Check Table 25 for degree of attenuation by adsorption-desorption for the chemical species of concern.
- Substitute appropriate adsorption K_D values into transport equations in previous section for appropriate group.

Table 25 divides the major constituents of concern present in geothermal fluid into three groups--not adsorbed, reversibly adsorbed, and irreversibly bound, to indicate the general extent of attenuation. Conservative species are not adsorbed by soil or mineral particles to any significant extent and are affected primarily by dispersive processes, i.e., advection, dilution, dispersion, proton exchange reactions, and to varying extents microbial conversion. Microbial activity is strongest in organic soils near the ground surface. Total dissolved solids may be treated as a conservative substance.

Adsorption and ion-exchange can be considered simultaneously. The preference of a soil particle for a given ion or adsorbate depends on type of soil and relative concentration of the species in the soil solution. Generally multivalent ions are adsorbed more strongly than monovalent ions and hence are less mobile in soil water systems. The cation preference is described by



a

b

c

Figure 19. Graphical solution for Wilson and Miller's equations (after Wilson and Miller, 1978).

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TABLE 25. GENERAL ADSORPTION-DESORPTION BEHAVIOR OF SELECTED AQUEOUS CHEMICAL SPECIES

Constituents	Not Adsorbed	Adsorbed	Irreversibly Bound**
Total dissolved solids	X		
Aluminum (Al(aq))		X	
*Ammonia (NH_4^+)		X	
Arsenic ($HA_sO_4^{2-}$, $H_2A_sO_4^-$)		X	
Barium (Ba^{2+})		X	
Boron (H_3BO_3)		X	
Cadmium (Cd,II)		X	
Chloride (Cl^-)	X		
Fluoride (F^-)		X	
Copper (Cu (II))		X	
*Hydrogen sulfide (H_2S,HS^-)	X		
*Iron (Fe (II),(III))		X	
Lead (Pb (II))		X	
Lithium (Li^+)		X	
Magnesium (Mg^{2+})		X	
*Manganese (Mn (II),(IV))		X	
Selenium (SeO_3^{2-})		X	
Silver (Ag^+)		X	
Zinc (Zn (II))		X	
Mercury (Hg (II))		X	
Molybdenum (molybdic acid)		X	
Sodium (Na^+)	X		
*Nitrate (NO_3^-)	X		
Calcium (Ca^{2+})		X	
Carbonate (CO_3^{2-})		X	
Silica (silicic acid)			X
Sulfate (SO_4^{2-})		X	
Chromium (Cr (III) (VI))		X	

*These species are susceptible to microbially mediated biochemical conversions (e.g., oxidation-reduction). The greatest density (and activity) of soil microflora occurs near the ground surface in organic soil horizons.

**Very strongly bound.

selectivity and exchange coefficients in the following equations (Bolt and Bruggenwert, 1976):

For ions of equal valence,

$$\frac{\overset{+}{\gamma}_a}{\overset{+}{\gamma}_b} = K_{a/b} \frac{C_{o,a}}{C_{o,b}} \tag{26}$$

where $K_{a/b}$ = Kerr selectivity coefficient (values given in Appendix C)

$\overset{+}{\gamma}_a$ = amount of ion "a" on (bound to) the soil solid phase, meq/100 grams soil

$\overset{+}{\gamma}_b$ = amount of ion "b" on (bound to) the soil solid phase, meq/100 grams soil

$C_{o,a}$ = concentration of ion "a" in soil solution, meq/kg solution

$C_{o,b}$ = concentration of ion "b" in soil solution, meq/kg solution

For monovalent/divalent ion preference

$$\frac{\overset{+}{\gamma}_+}{\overset{+}{\gamma}_{2+}} = \frac{K_G \, C_{o,1+}}{\sqrt{\frac{C_{o,2+}}{2}}} \tag{27}$$

where $\overset{+}{\gamma}_+$ = amount of monovalent cation on (bound to) the soil solid phase, meq/100 g soil

$\overset{+}{\gamma}_{2+}$ = amount of divalent cation on (bound to) the soil solid phase, meq/100 g soil

K_G = Gapon exchange constant in Appendix C

$C_{o,1+}$ = concentration of monovalent cation in soil solution, meq/kg solution

$C_{o,2+}$ = concentration of divalent cation in soil solution, meq/kg solution

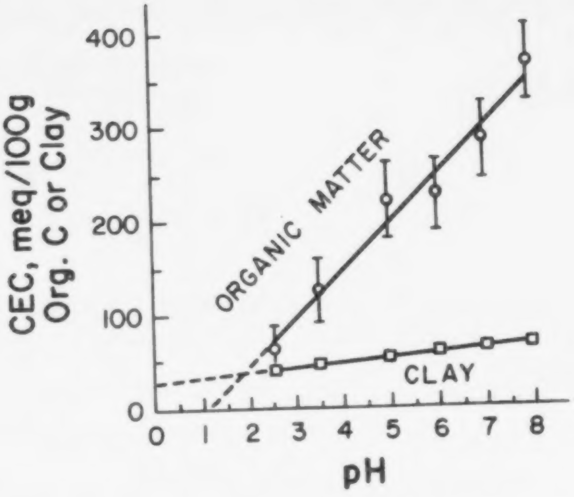
Preferences for several soil components are given below, with the most strongly bound (least mobile) constituents appearing on the left:

Exchange Medium	Cations
Clays	$\mathrm{Ca>Mg>Ba=Sr=Zn=Co=Ni=Cu}$
	$\mathrm{Cs>Rb>K \simeq NH_4>Na>Li}$
Iron and aluminum oxides	$\mathrm{Li>Na>NH_4>K>Rb>Cs}$
Organic material	$\mathrm{Cu>Fe^{3+} \simeq Pb^{2+}>Ni \simeq Co \simeq Mn}$
	Anions
Clays, iron and aluminum oxides	$\mathrm{SiO_4>PO_4>>SO_4>NO_3>>Cl}$

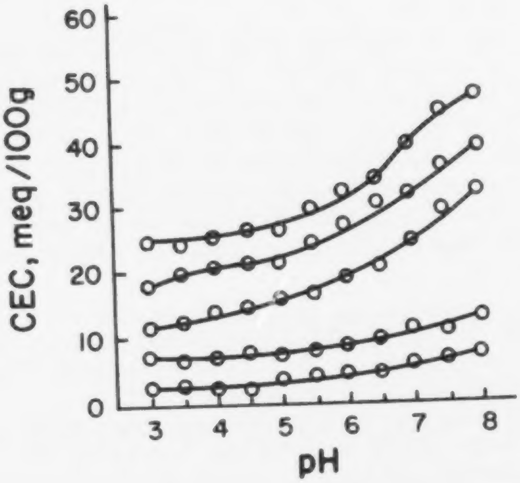
Cation exchange capacity (CEC) of a soil is the total amount of cations which can be exchanged per unit mass of soil (milliequivalents/100 grams soil). Clay minerals and organic matter contribute most of the CEC. The clay minerals also provide the bulk of the soil specific surface area. CEC's of clays range from 3-6 meq/100 g for micas to 200-300 meq/100 g for montmorillonites. CEC's of soil organic matter are typically of the order of 100-400 meq/l. Appendix B gives representative CEC values for different soils. As shown in Figure 20, CEC varies with pH. If site-specific measurements are not available, you may select a value similar in pH and soil composition. Anion exchange capacity (AEC) is the amount of anions which can be exchanged. The AEC typically ranges from 1 to 5% of the CEC for most soils. For saline soils the AEC may be 10-15% of the CEC (Bolt and Bruggenwert, 1976).

Specific adsorption includes reactions which result in insoluble compounds or tightly-bound complexes. This type of adsorption can be a function of pH and the concentration of complexing agents (i.e., $\mathrm{Cl^-}$) and organic matter (Figure 21). Many metals in aqueous solution have characteristic "adsorption edge" pH values where adsorption increases sharply with increasing pH (Figure 22). Examples of metals which form chloride complexes include mercury, cadmium, and zinc. Manganese and copper readily form organic complexes. Chemical species such as fluoride and arsenic are specifically adsorbed on iron and aluminum compounds.

Species which become "irreversibly bound" are adsorbed so strongly that the concentration of the species in solution after moving through a short depth of soil may become very small. This group includes for example silica and phosphorus (orthophosphate form).



a. Cation-exchange capacities of organic matter and clay in 60 Wisconsin Soils.



b. Cation-exchange capacities for a group of acid California soils.

Figure 20. Cation-exchange capacity variations with pH (a. after Helling, 1964; b. after Coleman and Thomas, 1965).

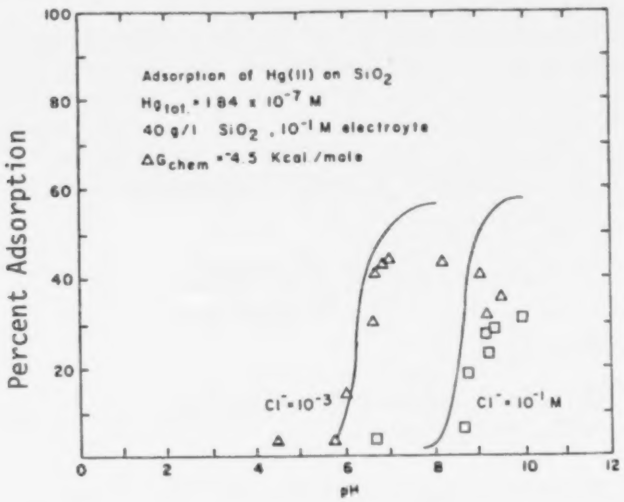
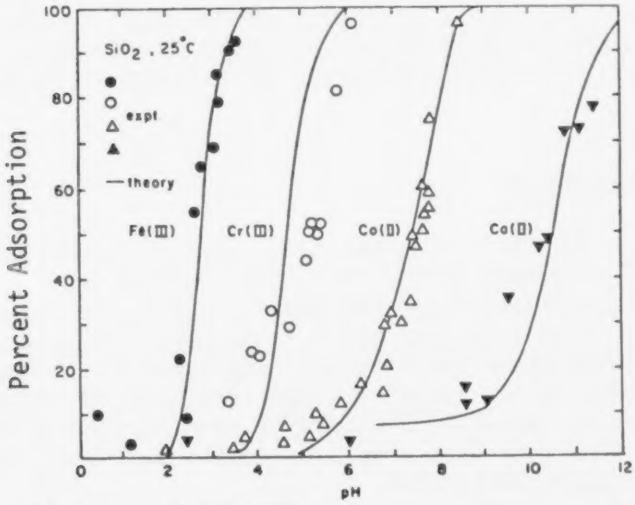


Figure 21. Effect of chloride concentration on adsorption of mercury (Rubin, 1976 used with permission of Ann Arbor Science Publishers).



Concentrations were:

Fe^{3+}	1.2 x 10^{-4} M	Co^{2+}	1.2 x 10^{-4} M
Cr^{3+}	2.0 x 10^{-4} M	Ca^{2+}	1.4 x 10^{-4} M

Figure 22. Effect of pH on adsorption of metals (Rubin, 1976 used with permission of Ann Arbor Science Publishers).

Calculation of Concentrations with Attenuation--

As an alternative to solving a series of exchange equations for each parameter simultaneously, you may determine the equivalent adsorption coefficient, K_D value, and substitute this into the appropriate transport equations described in the previous section. This procedure works well especially for the more dilute species. The "adsorption coefficient" (K_D) is an empirically-determined coefficient for a specific chemical species.

$$K_D = \frac{[C_{sorbed}]}{[C_{solution}]} \qquad (28)$$

where C_{sorbed} = pollutant concentration sorbed on soil, mg/kg soil

$C_{solution}$ = pollutant concentration in solution, mg/ℓ

In general, the K_D value is a function of chemical species, type of mineral phases present, pH, Cl^- ion concentration, and amount of organic matter present. For some species such as mercury, K_D can be expressed as a function of chloride concentration, pH, and soil specific surface area. Appendix C includes K_D values for selected chemical species. The effect of adsorption on transport of pollutants was tested using the GEOHY-GEOQAL model (Gherini, 1975). Figure 23 shows the decrease in amount of pollutant reaching a depth of two feet and six feet when adsorption is included (note the use of log scales).

EVALUATION OF SIGNIFICANCE

The final step in the procedure is to identify significant ground water contamination. The concentrations in usable aquifers at the plant boundary are compared with the pertinent water quality standards and regulations covering effluents from injection wells. The proposed Underground Injection Control Program mandated by the Safe Drinking Water Act protects aquifers with total dissolved solids concentrations less than 10,000 mg/ℓ. Aquifers protected under these regulations should be considered a potential drinking water source and concentrations should be compared to the present drinking water quality standards (Table 26).

The concentrations of constituents analyzed as conservative substances represent a worst case since no attenuation is considered. These resulting concentrations serve as upper bounds. If no standards are exceeded under these conditions, then ground water contamination would not be considered significant. If the concentrations of any constituents for the conservative case exceed standards, the concentrations with attenuation must be predicted and evaluated.

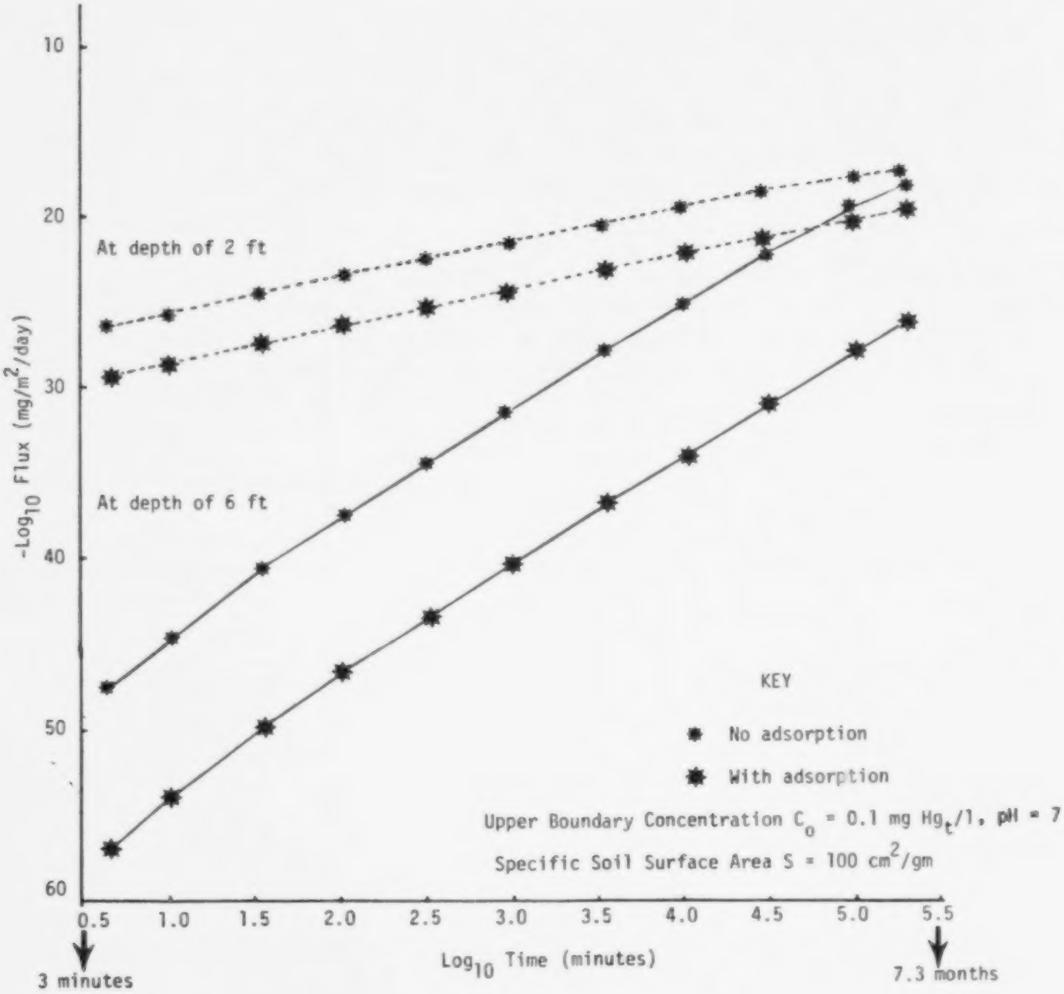


Figure 23. Effect of adsorption on mercury transport (after Gherini, 1975).

TABLE 26. U.S. EPA DRINKING WATER QUALITY STANDARDS (EPA, 1977a AND b)

Constituents	Annual average maximum daily air temperature °F	°C	Maximum level†
PRIMARY STANDARDS			
Inorganic Chemicals			
Arsenic			0.05
Barium			1.
Cadmium			0.010
Chromium			0.05
Lead			0.05
Mercury			0.002
Nitrate (as N)			10.
Selenium			0.01
Silver			0.05
Fluoride	53.7 and below	12.0 and below	2.4
	53.8 to 58.3	12.1 to 14.6	2.2
	58.4 to 63.8	14.7 to 17.6	2.0
	63.9 to 70.6	17.7 to 21.4	1.8
	70.7 to 79.2	21.5 to 26.2	1.6
	79.3 to 90.5	26.3 to 32.5	1.4
Radioactive Material			
Combined radium 226 and radium 228			5 pCi/l
Gross alpha particle activity			15 pCi/l
Beta particle and photon radioactivity from man-made radionuclides			4 millirem/year
Tritium			20,000 pCi/l
Strontium-90			8 pCi/l
SECONDARY STANDARDS			
Chloride			250.0
Color			15.0 c.u.
Copper			1.0
Methylene blue active substances			0.5
H_2S			0.05
Iron			0.3
Manganese			0.05
Odor			Threshold Order No. 3
pH			6.5 - 8.5
Sulphate			250.0
Total Dissolved Solids			500.0
Zinc			5.0
Corrosion			No maximum level but should reduce tendency for corrosion

†Units are mg/ℓ unless otherwise stated.

LIMITATIONS OF THE METHODOLOGY

The methodology presented in this manual has certain limitations. To make the methodology simple enough for desk top (non-computer) use, analytical rather than numerical solutions were adopted. This results in some loss in accuracy but a gain in ease of application. The analytical solutions are designed for ground water systems with uniform properties such as porosity and flow field. At a complex site the aquifer characteristics may change over short distances, particularly if the area is faulted. Solving the case for a realistic range of data values would provide likely ranges of constituent concentrations. The purpose of the methodology is to provide preliminary estimates so the information obtained for the range of data would be useful. We believe this use of analytical solutions is appropriate for a screening procedure.

For many of the variables used in the methodology there is a preference for field values as compared to laboratory or literature values. For example, dispersion as measured in soil columns in the laboratory usually underestimates the dispersion which occurs in aquifers due to lateral and vertical inhomogeneities. Better estimates can be obtained using tracer tests in the field. Porosity may be estimated from soil samples but may not be representative of the entire aquifer. Well logging with neutron logs may be helpful in estimating a representative porosity.

Appropriate pollutant adsorption values (K_D) may be difficult to obtain for some constituents. This is an area where further research would be most valuable.

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APPENDIX A

SOLUBILITY DATA

EQUILIBRIUM CONSTANTS

Equilibrium constants can be defined for reactions in dilute solutions as follows:

$$wA + xB = yC + zD, \text{ and}$$

$$K = \frac{[C]^y\ [D]^z}{[A]^w\ [B]^x}$$

where [C], [D], [A], [B] = molar concentrations of species A, B, C, and D

w, x, y, z = stoichiometric coefficients

In more concentrated solutions the effects of ionic interactions become more significant and species' activities (concentrations times activity coefficients) replace the concentrations in the above equation. The equilibrium constant is then referred to as K°.

For the case of equilibrium between a solid and its dissolved components the reaction is written with the solid on the left. The equilibrium constant is then referred to as a solubility product, K_{so}, where

$$A_xB_y(s) = xA + yB, \text{ and}$$

$$[A]^x\ [B]^y = K_{so}$$

where [A], [B] = molar concentrations of A and B

x, y = stoichiometric coefficients

(s) = solid phase

The concentration and activity of a solid are exactly unity.

For reactions involving dissociation of chemical species the equilibrium constants are called ionization constants or dissociation constants, K_A. For example, for the dissociation of diprotic acids the reactions are written in the following manner:

$$H_x L = H_y L^- + H^+$$

$$\frac{[H]^+ [H_y L^-]}{[H_x L]} = K_{A_1}$$

where: $[H^+]$ = molar concentration of hydrogen ion
$[H_y L^-]$ = molar concentration of $H_y L^-$
$[H_y L]$ = molar concentration of undissociated acid

Reactions involving the formation of complex ions are written in a similar manner as follows:

$$xA + yB = A_x B_y^m$$

$$\frac{[A_x B_y^m]}{[A]^x [B]^y} = K$$

where: $[A_x B_y^m]$ = molar concentration of complex ion
$[A],[B]$ = molar concentration of ions
x, y = stochiometric
m = charge of the complex coefficients

Molar concentrations are corrected for ionic strength by multiplying the concentration by an activity coefficient. The corrected concentration is then referred to as the activity. The activity coefficient can be estimated using the extended form of the Debye-Huckel equation (Bolt and Bruggenwert, 1976):

$$-\log f_i = \frac{A z_i^2 \sqrt{I}}{1 + a_i^\circ B \sqrt{I}}$$

where: f_i = activity coefficient of species i

z_i = charge on species i

I = $\frac{1}{2} \Sigma m_i z_i^2$, ionic strength

m = molar concentration of species i

a_i° = ionic size parameter

A,B = constants: at 25°C $A = .51\ (\text{mol}/\ell)^{-.5}$,
$B = .33\ A^{\circ -1}\ \text{mole}^{-0.5}\ \text{liter}^{0.5}$

Values of a_i° for selected chemical species are listed in Table A-1. Activity coefficients f_i, for a_i° values between 3 and 11 and for ionic strengths between 0.001 and 0.1 are listed in Table A-2. Ionic strength versus activity coefficients for several species are plotted in Figure A-1.

Data have been compiled for the chemical species listed in Table 25. The organization of the data is:

Table A-3. Solubility Products

Table A-4. Equilibrium Constants

Table A-5. Carbonate Equilibria Constants

Table A-6. Dissociation Constants of Acids

Table A-7. Formation Constants for Complex Ions

Most of the data apply to conditions of 25°C and atmospheric pressure. The effect of temperature on the equilibrium constants for several dissolved species is shown in Figure A-2.

TABLE A-1. VALUES OF THE IONIC SIZE PARAMETER å FOR SELECTED IONS

Charge	å	Ions
1	9	H^+
	8	$(C_6H_5)_2\ CHCOO^-$, $(C_3H_7)_4N^+$
	7	$OC_6H_2(NO_3)_3^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4COO^-$
	6	Li^+, $C_6H_5COO^-$, $C_6H_4OHCOO^-$, $C_6H_4ClCOO^-$, $C_6H_5CH_2COO^-$, $CH_2CHCH_2COO^-$, $(CH_3)_2CCHCOO^-$, $(C_2H_5)_4N^+$, $(C_3H_7)_2NH_2^+$
	5	$CHCl_2COO^-$, CCl_3COO^-, $(C_2H_5)_3NH^+$, $(C_3H_7)NH_3^+$
	4 - 4.5	Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, CH_3COO^-, CH_2ClCOO^-, $(CH_3)_4N^+$, $(C_2H_5)_2NH_2^+$, $NH_2CH_2COO^-$, $^+NH_3CH_2COOH$, $(CH_3)_3NH^+$, $C_2H_5NH_3^+$
	3.5	OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-
	3	CNS^-, CNO^-, ClO_3^-, ClO_4^-, K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$, $H_2(citrate)^-$, $CH_3NH_3^+$, $(CH_3)_2\ NH_2^+$
	2.5	Rb^+, Cs^+, NH_4^+, Ti^+, Ag^+
2	8	Mg^{2+}, Be^{2+}
	7	$(CH_2)_5(COO)_2^{2-}$, $(CH_2)_6(COO)_2^{2-}$
	6	Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(COO)_2^{2-}$, $H_2C(CH_2COO)_2^{2-}$, $(CH_2CH_2COO)_2^{2-}$
	5	Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, SO_3^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $H_2C(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $(CHOHCOO)_2^{2-}$, $(COO)_2^{2-}$, $H(citrate)^{2-}$
	4.5	Pb^{2+}, CO_3^{2-}, SO_4^{2-}, MoO_4^{2-}
	4	Hg_2^{2+}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, $S_2O_6^{2-}$, PO_4^{3-}

(continued)

TABLE A-1 (continued)

Charge	$\mathring{a}$	Ions
3	9	Al^{3+}, Fe^{3+}, Cr^{3+}, Se^{3+}, Y^{3+}, La^{3+}, Ln^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}
	6	$Co(ethylenediamine)_3^{3+}$
	5	$Citrate^{3-}$
	4	PO_4^{3-}, $Fe\left(CN\right)_6^{3-}$, $Cr\left(NH_3\right)_6^{3+}$, $Co\left(NH_3\right)_6^{3+}$, $Co\left(NH_3\right)_5H_2O^{3+}$
4	11	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}
	6	$Co\left(S_2O_3\right)\left(CN\right)_5^{4-}$

Source: Kielland, 1937 and Klotz, 1950

TABLE A-2. SINGLE-ION ACTIVITY COEFFICIENTS CALCULATED FROM THE EXTENDED DEBYE-HÜCKEL EQUATION AT 25°C

Activity Coefficients

Charge	Ionic strength $\mathring{a}$	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
1	9	0.967	0.950	0.933	0.914	0.88	0.86	0.83
	8	0.966	0.949	0.931	0.912	0.88	0.85	0.82
	7	0.965	0.948	0.930	0.909	0.875	0.845	0.81
	6	0.965	0.948	0.929	0.907	0.87	0.835	0.80
	5	0.964	0.947	0.928	0.904	0.865	0.83	0.79
	4	0.964	0.947	0.927	0.901	0.855	0.815	0.77
	3	0.964	0.945	0.925	0.899	0.85	0.805	0.755
2	8	0.872	0.813	0.755	0.69	0.595	0.52	0.45
	7	0.872	0.812	0.753	0.685	0.58	0.50	0.425
	6	0.870	0.809	0.749	0.675	0.57	0.485	0.405
	5	0.868	0.805	0.744	0.67	0.555	0.465	0.38
	4	0.867	0.803	0.740	0.660	0.545	0.445	0.355
3	9	0.738	0.632	0.54	0.445	0.325	0.245	0.18
	6	0.731	0.620	0.52	0.415	0.28	0.195	0.13
	5	0.728	0.616	0.51	0.405	0.27	0.18	0.115
	4	0.725	0.612	0.505	0.395	0.25	0.16	0.095
4	11	0.588	0.455	0.35	0.255	0.155	0.10	0.065
	6	0.575	0.43	0.315	0.21	0.105	0.055	0.027
	5	0.57	0.425	0.31	0.20	0.10	0.048	0.021

Source: Bolt and Bruggenwert, 1976

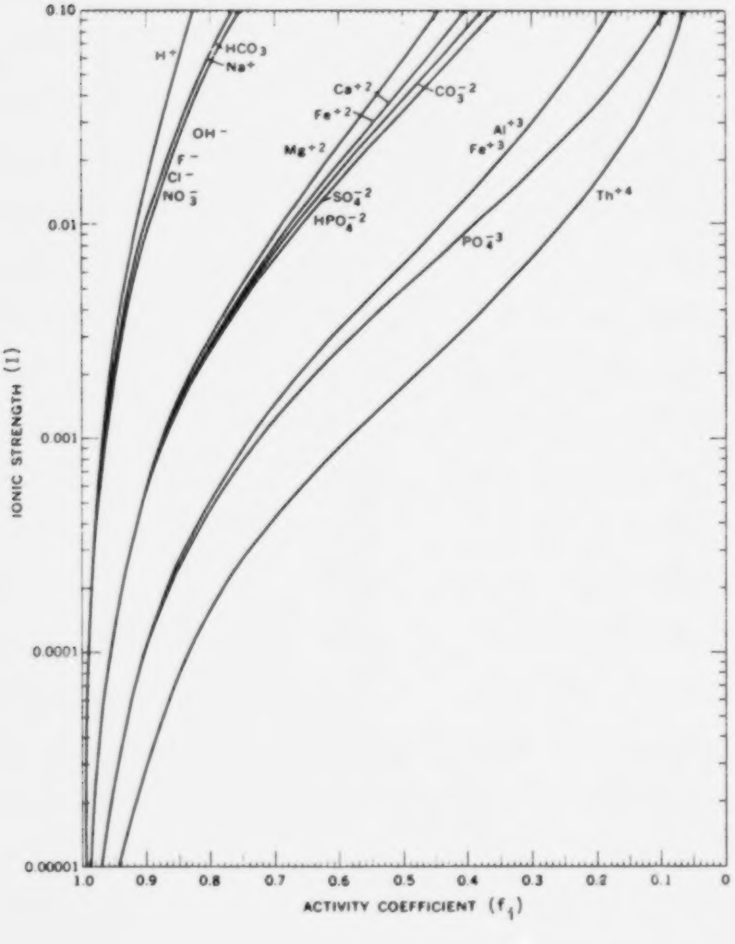


Figure A-1. Activity coefficients as a function of ionic strength for selected dissolved ions (Hem, 1970).

TABLE A-3. SELECTED SOLUBILITY PRODUCTS

Reaction*	T°C	Ionic strength	Log $K^{*\dagger\dagger}_{so}$	Reference
$Al(OH)_3(s) =^{\dagger} Al^{3+} + 3OH^-$	25		- 32.34	1
$AlPO_4 \cdot 2H_2O(s) = Al^{3+} + H_2PO_4^- + 2OH^-$	25	0	- 30.50	1
$NH_3(g) + H_2O = NH_4OH$	25		+ 1.75	1
$BaCO_3(s) = Ba^{2+} + CO_3^{2-}$	25	0	- 8.2	3
$BaSeO_4(s) = Ba^{2+} + SeO_4^{2-}$	25	Dilute	- 7.46	3
$CdSeO_3(s) = Cd^{2+} + SeO_3^{2-}$	20		- 8.9	3
$CdCO_3(s) = Cd^{2+} + CO_3^{2-}$	25	0	- 13.74	4
$Cd(OH)_2(s) = Cd^{2+} + 2OH^-$	25	0	- 13.79	4
$CdCO_3(s) + 2H^+ = Cd^{2+} + H_2O + CO_2(g)$	25	0	- 6.14	3
$CdS(s) = Cd^{2+} + S^{2-}$	25		- 27.2	4
$CaSO_4 \cdot 2H_2O(s) = Ca^{2+} + SO_4^{2-} + 2H_2O$	25	0	- 4.61	2
$CaF_2(s) = Ca^{2+} + 2F^-$	25		- 10.57	2
$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ (calcite)	25	0	- 8.22	1
$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ (aragonite)	25	0	- 8.35	1
$CaMg(CO_3)_2(s) = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	25	0	- 16.90	1
$Ca(H_2PO_4)_2 \cdot H_2O(s) = Ca^{2+} + 2H_2PO_4^- + H^2O$	25	0	- 1.14	1
$CaHPO_4 \cdot 2H_2O(s) = Ca^{2+} + HPO_4^{2-} + 2H_2O$	25	0	- 6.56	1
$CaHPO_4(s) = Ca^{2+} + HPO_4^{2-}$	25	0	- 6.66	1
$Ca_4H(PO_4) \cdot 3H_2O(s) = 4Ca^{2+} + H^+ + 3PO_4^{3-} + 3H_2O$	25	0	- 46.91	1
$Ca_3(PO_4)_2(s) = 3Ca^{2+} + 2PO_4^{3-}$	25	0	- 26.00	1
$Ca_{10}(PO_4)_6(OH)_2(s) = 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	25	0	-113.7	1
$Ca_{10}(PO_4)_6(F)_2(s) = 10Ca^{2+} + 6PO_4^{3-} + 2F^-$	25	0	-120.86	1
$Ca_3(AsO_4)_2(s) = 3Ca^{2+} + 2(AsO_4)^{3-}$	20		- 18.2	3
$CaSeO_3(s) = Ca^{2+} + SeO_3^{2-}$	20		- 5.53	3
$CaSeO_4(s) = Ca^{2+} + SeO_4^{2-}$	25	0	- 3.09	3

(continued)

TABLE A-3 (continued)

Reaction*	T°C	Ionic strength	Log K°_{so}††	Reference
$CaMoO_4(s) = Ca^{2+} + MoO_4{}^{2-}$	25	0	- 8	3
$Cu_3(AsO_4)_2(s) = 3Cu^{2+} + 2AsO_4{}^{3-}$	20		- 35.1	3
$CuCrO_4(s) = Cu^{2+} + CrO_4{}^{2-}$	25	0	- 5.44	3
$CuSeO_3(s) = Cu^{2+} + SeO_3{}^{2-}$	20		- 7.68	3
$CuO(s) + 2H^{+} = Cu^{2+} + H_2O$	25	0	7.65	2
$Cu(OH)(CO_3)_{0.5}(s) + 2H^{+} = Cu^{2+} + \frac{3}{2}H_2O + 1/2CO_2(g)$	25	0	7.08	2
$Cu(OH)_{0.67}(CO_3)_{0.67}(s) + 2H^{+} =$ $Cu^{2+} + \frac{4}{3}H_2O + \frac{2}{3}CO_2(g)$	25	0	7.08	2
$Fe(OH_3(s) = Fe^{3+} + 3OH^{-}$	25		- 37.5**	1
$Fe(OH)_3(s) = Fe^{3+} + 3OH^{-}$	25		- 39.1**	1
$1/2\alpha\text{-}Fe_2O_3(s) + 3/2H_2O = Fe^{3+} + 3OH^{-}$	25	0	- 42.5	1
$\alpha\text{-}FeOOH(s) + H_2O = Fe^{3+} + 3OH^{-}$	25	0	- 44.0	1
$Fe(OH)_2(s) = Fe^{2+} + 2OH^{-}$	25	0	- 15.1	1
$FePO_4 \cdot 2H_2O(s) = Fe^{3+} + H_2PO_4{}^{-} + 2OH^{-}$	25	0	- 34.9	1
$Fe_3(PO_4)_2 \cdot 8H_2O(s) = 3Fe^{2+} + 2PO_4{}^{3-} + 8H_2O$	25	0	- 36.0	1
$Fe_2(SeO_3)_3(s) = 2Fe^{2+} + 3(SeO_3)^{2-}$	20		- 30.7	1
$FeCO_3(s) = Fe^{2+} + CO^{2-}$	25		- 10.7	1
$am.FeOOH(s) + 3H^{+} = Fe^{3+} + 2H_2O$	25	3 $NaClO_4$	3.55	2
α - $FeOOH(s) + 3H^{+} = Fe^{3+} + 2H_2O$	25	3 $NaClO_4$	1.6	2
$FeA_sO_4(s) = Fe^{3+} + AsO_4{}^{3-}$	20		- 20.2	3
$PbCrO_4(s) = Pb^{2+} + CrO_4{}^{2-}$	25	Dilute	- 12.55	3
$PbSeO_4(s) = Pb^{2+} + SeO_4{}^{2-}$	25	0	- 6.84	3
$PbCO_3(s) = Pb^{2+} + CO_3{}^{2-}$	25		- 13.00	4
$Pb(OH)_2(s) = Pb^{2+} + 2OH^{-}$	25		- 14.93	4
$PbSO_4(s) = Pb^{2+} + SO_4{}^{2-}$	25		- 7.89	4

(continued)

TABLE A-3 (continued)

Reaction*	T°C	Ionic strength	Log K°_{so}††	Reference
$Pb_3(OH)_2(CO_3)_2(s) = 3Pb^{2+} + 2OH^- + 2CO_3$	25		- 18.80	4
$Mg_3(AsO_4)_2(s) = 3Mg^{2+} + 2(AsO_4)^{3-}$	20		- 19.7	3
$Mg(OH)_2(s) = Mg^{2+} + 2OH$	25	0	- 10.8	3
$MgSeO_3(s) = Mg^{2+} + SeO_3{}^{2-}$	20		- 4.89	3
$MgCO_3(s) = Mg^{2+} + CO_3{}^{2-}$	25		- 7.80	1
$MnS(s) = Mn^{2+} + S^{2-}$ (precipitate)	25		15.7	4
$Mn_3(AsO_4)_2(s) = 3Mn^{2+} + 2(AsO_4)^{3-}$	20	Dilute	- 28.7	3
$MnCO_3(s) = Mn^{2+} + CO_3{}^{2-}$	25	Dilute	- 9.4	3
$Mn(OH)_2(s) = Mn^{2+} + 2OH$	25	0	- 12.8	3
$MnSeO_3(s) = Mn^{2+} + SeO_3{}^{2-}$	20		- 6.9	3
$Hg_2SO_4(s) = Hg_2{}^{+} + SO_4{}^{2-}$	25	0	- 6.2	3
$HgO(s) + H_2O = Hg(OH)_2$ (aq)			- 3.7	4
$HgO(s) + H_2O = Hg^{2+} + 2OH$			- 25.7	4
$HgCl_2(s) = Hg^{2+} + 2Cl$			- 13.8	4
$Hg_2Cl_2(s) = Hg_2{}^{2+} + 2Cl^-$			- 18.00	4
$HgCrO_4(s) = Hg^{2+} + CrO_4{}^{2-}$	25	0	- 8.7	3
$HgS(s) = Hg^{2+} + S^{2-}$	25			
(metacinnabar)			- 52.2	4
(cinnabar)			- 53.6	4
$Ag_3AsO_4(s) = 3Ag^{1+} + AsO_4{}^{3-}$	20	Dilute	- 19.95	3
$Ag_2CO_3(s) = 2Ag^{1+} + CO_3{}^{2-}$	25	0	- 11.2	3
$AgCl(s) = Ag^{1+} + Cl^-$	25	0	- 9.7	3
$2AgCrO_4(s) = 2Ag^{1+} + CrO_4{}^{2-}$	25	0	- 11.89	3
$Ag(OH)(s) = Ag^{1+} + OH^-$	25	0	- 7.6	3
$Ag_2MoO_4(s) = 2Ag^{1+} + MoO_4{}^{2-}$	25	0	- 11.55	3

(continued)

TABLE A-3 (continued)

Reaction*	T°C	Ionic strength	Log $K^{\circ\dagger\dagger}_{so}$	Reference
$Ag_2SeO_3(s) = 2Ag^+ + SeO_3^{2-}$	20	0	- 14.74	3
$Ag_2SeO_4(s) = 2Ag^+ + SeO_4^{2-}$	25	0	- 8.91	3
$SrSeO_4(s) = Sr^{2+} + SeO_4^{2-}$	25	0	- 4.6	3
$Zn_3(AsO_4)_2(s) = 3Zn^{2+} + 2(AsO_4)^{3-}$	20	Dilute	- 26.97	3
$ZnSeO_3(s) = Zn^{2+} + SeO_3^{2-}$	20		- 6.59	3
$ZnCO_3(s) = Zn^{2+} + CO_3^{2-}$			- 10.00	4
$Zn(OH)_2(s) = Zn^{2+} + 2OH^-$			- 15.52	4
$ZnS(s) = Zn^{2+} + S^{2-}$ (precipitate)	25	0	- 22.05	4
$Zn_3(PO_4)_2\ 4H_2O(s) = 3Zn^{2+} + 2PO_4^{3-} + 4H_2O$			- 32.04**	1
$ZnO(s) + 2H^+ = Zn^{2+} + H_2O$	25	0	11.18	2
$ZnCO_3(s) + 2H^+ = Zn^{2+} + H_2O + CO_2(g)$	25	0	7.95	2
$Zn(OH)_{1.2}(CO_3)_{0.4}(s) + 2H^+ =$ $Zn^{2+} + 1.6\ H_2O + 0.4\ CO_2(g)$	25	0	9.80	2

*(s) = solid phase.

**Conditions noted only as not 25°C or Ionic Strength = 0

†Equal sign means reversible reaction.

††K°_{so}, solubility product for use with activities.

References:
1 - Bolt and Bruggenwert, 1976
2 - Schindler, 1967
3 - Sillen and Martel, 1964
4 - Rubin, 1976

Note: A blank under temperature or ionic strength indicates that conditions were not given. All pressures = 1 atm.

TABLE A-4. SELECTED EQUILIBRIUM CONSTANTS

Reaction	T°C	Ionic strength	Log $\overset{\circ}{K}$	Reference
$Al^{3+} + 4OH^- =^{+}Al(OH)_4^-$	25	0	32.5	2
$Al^{3+} + F^- = AlF^{2+}$	25	0.53 KNO_3	6.13	2
$Al^{3+} + 2F^- = AlF_2^+$	25	0.53 KNO_3	11.15	2
$Al^{3+} + 3F^- = AlF_3$	25	0.53 KNO_3	15.00	2
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	30	0	2.04	2
$NH_3(g) + H_2O = NH_4OH$	25		1.75	1
$Ba^+ + OH = BaOH$	25	0	0.64	3
$Ba^+ + SO_4^- = BaSO_4$	25		- 10	1
$Cd^{2+} + OH^- = CdOH^+$	25	3 $LiClO_4$	3.8	2
$Cd^{2+} + F^- = CdF^+$	25	1 $NaClO_4$	0.46	2
$Cd^{2+} + Cl^- = CdCl^+$	25	0	2.00	2
$Cd^{2+} + 2Cl = CdCl_2$	25	0	2.70	2
$Cd^{2+} + 3Cl^- = CdCl_3^-$	25	0	2.11	2
$Cd^{2+} + Br^- = CdBr^+$	25	0	2.15	2
$Cd^{2+} + SO_4^{2-} = CdSO_4$	25	0	2.29	2
$Cd^{2+} + SeO_4^{2-} = CdSeO_4$	25	0	2.27	3
$Ca^{2+} + F^- = CaF^+$	25	0	1.04	2
$Sr^{2+} + CaCO_3(s,calcite) = (Ca_{x1},Sr_{x2})CO_3 + Ca^{2+}$ $\left(= \log\left(x_2\frac{[Ca^{2+}]}{[Sr^{2+}]}\right)\right)$	25	Dilute	- 0.89	2
$Cu^{2+} + OH^- = CuOH^+$	18	0	6.0	2
$2Cu^{2+} + 2OH^- = Cu_2(OH)_2^{2+}$	18	0	17.0	2
$Cu^{2+} + 3OH^- = Cu(OH)_3^-$	25	0	15.2	2

(continued)

TABLE A-4 (continued)

Reaction	T°C	Ionic strength	Log $\overset{\circ}{K}$	Reference
$Cu^{2+} + 4OH^- = Cu(OH)_4{}^{2-}$	25	0	16.1	2
$Cu^{2+} + F^- = CuF^+$	25	0.5 $NaClO_4$	1.23	2
$Cu^{2+} + Cl^- = CuCl^+$	22	0	0	2
$Cu^{2+} + SO_4{}^{2-} = CuSO_4$	25	0	2.3	2
$Cu^{2+} + CO_3 = CuCO_3$	25	0	6.77	2
$Cu^{2+} + 2CO_3{}^{2-} = Cu(CO_3)_2{}^{2-}$	25	0	10.01	2
$Cr^{+3} + Cl_3 = CrCl_3$	25	0	0.60	3
$Fe^{3+} + 3F^- = FeF_3$	25	0.5 $NaClO_4$	12.00	2
$Fe^{3+} + Cl^- = FeCl^{2+}$	25	1 $HClO_4$	0.46	2
$Fe^{3+} + SO_4{}^{2-} = FeSO_4{}^+$	25	0.5 $NaClO_4$	2.31	2
$Fe^{3+} + OH^- = FeOH^{2+}$	25	3 $NaClO_4$	11.17	2
$Fe^{3+} + 2OH^- = Fe(OH)_2{}^+$	25	3 $NaClO_4$	22.13	2
$Fe^{3+} + 4OH^- = Fe(OH)_4{}^-$	25	3 $NaClO_4$	34.11	2
$Fe^{3+} + F^- = FeF^{2+}$	25	0.5 $NaClO_4$	5.17	2
$Fe^{3+} + 2F^- = FeF_2{}^+$	25	0.5 $NaClO_4$	9.09	2
$Fe^{2+} + SO_4{}^{2-} = FeSO_4$	25	0	2.3	3
$Pb^{2+} + SO_4{}^{2-} = PbSO_4$	25	0	2.62	3
$Li^{1+} + OH^- = LiOH$	25	0	0.13	3
$Li^{1+} + NO_3{}^- = LiNO_3$	30	0	- 1.45	3
$Mg^{2+} + OH^- = Mg(OH)_2$	25	0	1.4	3
$Mg^{2+} + SO_4{}^{2-} = MgSO_4$	25	0	2.36	3
$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$	25		16.78	1
$Mn^{2+} + OH^- = Mn(OH)_2$	25	Dilute	- 10.6	3
$Hg^{2+} + SeO_3{}^{2-} = HgSeO_3$	20		- 1.38	3

(continued)

TABLE A-4 (continued)

Reaction	T°C	Ionic strength	Log K°	Reference
$Ag^{1+} + OH^{-} = AgOH$	25	0	2.3	3
$Ag^{1+} + NO_3^{-} = AgNO_3$	25	0	- 0.24	3
$Ag^{1+} + SO_4^{2-} = AgSO_4^{-}$	25	3	0.23	3
$Ag^{1+} + Cl^{1-} = AgCl$	25	0	3.3	3
$Na^{1+} + OH^{-} = NaOH$	25	0	- 0.70	3
$Na^{1+} + CO_3^{-} = NaCO_3$	25	0	1.27	3
$Na^{1+} + SO_4^{2-} = NaSO_4^{-}$	25	0	0.72	3
$Na^{1+} + HCO_3^{-} = NaHCO_3$	25	0	- 0.25	3
$SiO_2(s) + 2H_2O = H_4SiO_4$ (amorphous SiO_2)			- 2.74	1
$SiO_2(s) + 2H_2O = H_4SiO_4$ (quartz)			- 4.00	1
$Zn^{2+} + OH^{-} = ZnOH^{+}$	25	0	5.04	1
$Zn^{2+} + 3OH^{-} = Zn(OH)_2^{-}$	25	0	13.9	1
$Zn^{2+} + 4OH^{-} = Zn(OH)_4^{2-}$	25	0	15.1	1
$Zn^{2+} + F^{-} = ZnF^{+}$	25	0	1.26	1
$Zn^{2+} + Cl^{-} = ZnCl^{+}$	25	0	0.43	1
$Zn^{2+} + 2Cl^{-} = ZnCl_2$	25	0	0.61	1
$Zn^{2+} + 3Cl^{-} = ZnCl_3^{-}$	25	0	0.53	1
$Zn^{2+} + 4Cl^{-} = ZnCl_4^{2-}$	25	0	0.20	1
$Zn^{2+} + SO_4^{2-} = ZnSO_4$	25	0	2.38	2
$Zn^{2+} + SeO_4^{2-} = ZnSeO_4$	25	0	2.19	3

All pressures = 1 atm.

†Equal sign means reversible reaction.

References:
1 - Bolt and Bruggenwert, 1976
2 - Schindler, 1967
3 - Sillen and Martel, 1964
4 - Rubin, 1976

Note: A blank under temperature or ionic strength indicates conditions were not given. All pressures = 1 atm.

TABLE A-5. CARBONATE SYSTEM EQUILIBRIUM CONSTANTS (AFTER GARRELS AND CHRIST, 1965)

Temperature, °C	pK_1 †	pK_2 ††	pK_3**	pK_{CO_2}***
0	6.58	10.62	8.02	1.12 (0.2°)
5	6.52	10.56	8.09	
10	6.47	10.49	8.15	
15	6.42	10.43	8.22	
20	6.38	10.38	8.28	
25	6.35	10.33	8.34	1.47
30	6.33	10.29	8.40	
40	6.30	10.22	8.52	1.64
50	6.29	10.17	8.63	
80	(6.32)	(10.12)	8.98	

† $pK_1 = -\log K_{H_2CO_3^*}$

†† $pK_2 = -\log K_{HCO_3}$

** $pK_3 = -\log K_{CaCO_3}$

*** $pK_{CO_2} = -\log K_{CO_2}$

where $K_{CO_2} = H_2CO_3^*/P_{CO_2}$ and

P_{CO_2} = the partial pressure of CO_2.

Values of original authors rounded to two decimal places in present table.

TABLE A-6. DISSOCIATION CONSTANTS OF ACIDS IN AQUEOUS SOLUTIONS (25°C)

Acid[†]	Name of acid	-Log acidity constant, pK_A (approximate)	Reference
$HClO_4$	Perchloric acid	-7	1
HCl	Hydrochloric acid	~-3	1
H_2SO_4	Sulfuric acid	~-3	1
HNO_3	Nitric acid	-1	1
H_3O^+	Hydronium ion	0	1
H_3PO_4	Phosphoric acid	2.1	1
$[Fe(H_2O)_6]^{3+}$	Aquo ferric ion	2.2	1
HF	Hydrofluoric acid	3.6	3
CH_3COOH	Acetic acid	4.7	1
$[Al(H_2O)_6]^{3+}$	Aquo aluminum ion	4.9	1
$H_2Mo_2O_7$	Molybdic acid	5	3
$H_2CO_3^*$	Aqueous carbon dioxide	6.3	1
$H_2Cr_2O_7$	Chromic acid	7	3
H_2S	Hydrogen sulfide	7.1	1
$H_2PO_4^-$	Dihydrogen phosphate	7.2	1
HPO_4^{2-}	Monohydrogen phosphate	7.2	3
$HOCl$	Hypochlorous acid	7.6	1
$HSeO_3^{2-}$	Selenious acid	8.3	3
$H_2As(OH)_4^-$	Arsenic acid	9.1	3
HCN	Hydrogen cyanide	9.2	1
H_3BO_3	Boric acid	9.3	1
NH_4^+	Ammonium ion	9.3	1
$Si(OH)_4$	O-Silicic acid	9.5	1
HCO_3^-	Bicarbonate	10.3	1
H_2O_2	Hydrogen peroxide	-	
$SiO(OH)_3^-$	Silicate	12.6	1

(continued)

TABLE A-6 (continued)

Acid[†]	Name of acid	-Log acidity constant, pK_A (approximate)	Reference
HS^-	Bisulfide	14	1
H_2O	Water	14	1
NH_3	Ammonia	~23	1
OH^-	Hydroxide ion	~24	1
CH_4	Methane	~34	1

[†] In order of decreasing strength (as measured by extent of dissociation).

References: 1 - Stumm and Morgan, 1970
3 - Sillen and Martel, 1964

TABLE A-7. FORMATION CONSTANTS OF SELECTED COMPLEX IONS

Reaction	Log $\overset{\circ}{K}$	Reference
$Al^{3+} + H_2PO_4^{-} = {}^{+}AlH_2PO_4^{2+}$	∼ 3*	1
$Al^{3+} + HPO_4^{2-} = AlHPO_4^{+}$	∼ 8.1*	1
$Al^{3+} + H_2O = AlOH^{2+} + H^{+}$	- 5.02	1
$Al^{3+} + 4H_2O = Al(OH)_4^{-} + 4H^{+}$	-23.57	1
$2Al^{3+} + 2H_2O = Al_2(OH)_2^{4+} + 2H^{+}$	- 6.27	1
$Ca^{2+} + H_2PO_4^{-} = CaH_2PO_4^{+}$	1.08	1
$Ca^{2+} + HPO_4^{2-} = CaHPO_4^{\circ}$	2.70	1
$Ca^{2+} + SO_4^{2-} = CaSO_4^{\circ}$	2.31	1
$Ca^{2+} + HCO_3^{-} = CaHCO_3^{+}$	1.26	1
$Ca^{2+} + CO_3^{2-} = CaCO_3^{\circ}$	3.20	1
$Cd^{2+} + OH^{-} = CdOH^{+}$	4.59	4
$Cd^{2+} + 2OH^{-} = Cd(OH)_2^{\circ}$	8.93	4
$Cd^{2+} + 3OH^{-} = Cd(OH)_3^{-}$	9.58	4
$Cd^{2+} + Cl^{-} = CdCl^{+}$	2.08	4
$Cd^{2+} + OH^{-} + Cl^{-} = CdOHCl^{\circ}$	5.87	4
$Cd^{2+} + SO_4^{=} = CdSO_4^{\circ}$	2.76	4
$Fe^{3+} + H_2O = FeOH^{2+} + H^{+}$	- 3.0*	1
$Fe^{3+} + 2H_2O = Fe(OH)_2^{+} + 2H^{+}$	- 6.4*	1
$2Fe^{3+} + 2H_2O = Fe_2(OH)_2^{4+} + 2H^{+}$	- 3.1*	1
$Fe^{3+} + 3H_2O = Fe(OH)_3^{\circ} + 3H^{+}$	-13.5*	1
$Fe^{3+} + 4H_2O = Fe(OH)_4^{-} + 4H^{+}$	-23.5*	1
$Fe^{2+} + H_2O = FeOH^{+} + H^{+}$	- 8.3	1
$Fe^{2+} + 2H_2O = Fe(OH)_2^{\circ} + 2H^{+}$	-17.2	1
$Fe^{2+} + 3H_2O = Fe(OH)_3^{-} + 3H^{+}$	-32.0	1

(continued)

TABLE A-7 (continued)

Reaction	Log K°	Reference
$Fe^{2+} + 4H_2O = Fe(OH)_4^{2-} + 4H^+$	-46.4	1
$Fe^{3+} + HPO_4^{2-} = FeHPO_4^+$	∿ 9.75*	1
$Pb^{2+} + OH^- = PbOH^+$	5.85	4
$Pb^{2+} + 2OH^- = Pb(OH)_2^\circ$	10.80	4
$Pb^{2+} + 3OH^- = Pb(OH)_3^-$	13.92	4
$Pb^{2+} + Cl^- = PbCl^+$	1.62	4
$Pb^{2+} + 2Cl^- = PbCl_2^\circ$	1.83	4
$Mg^{2+} + HCO_3^- = MgHCO_3^+$	1.16	1
$Mg^{2+} + CO_3^{2-} = MgCO_3^\circ$	3.40	1
$Hg^{2+} + H_2O = HgOH^+ + H^+$	- 3.4	4
$Hg^{2+} + 2H_2O = Hg(OH)_2^\circ + 2H^+$	- 6.00	4
$Hg^{2+} + 3H_2O = Hg(OH)_3^- + 3H^+$	-20.7	4
$Hg^{2+} + Cl^- = HgCl^+$	6.7	4
$Hg^{2+} + 2Cl^- = HgCl_2^\circ$	13.2	4
$Hg^{2+} + 3Cl^- = HgCl_3^-$	14.2	4
$Hg^{2+} + 4Cl^- = HgCl_4^{2-}$	15.2	4
$HgCl_2^\circ + H_2O = HgOHCl^\circ + Cl^- + H^+$	- 9.6	4
$HgCl_2 + 2H_2O = Hg(OH)_2^\circ + 2Cl^- + 2H^+$	-19.6	4
$Hg^{2+} + Cys = HgCys^{2+}$ (Cys = Cysteine)	43.57	4
$Hg^{2+} + Gly^- = (HgGly)^+$ (Gly = Glycine)	10.3	4
$(HgGly)^+ + Gly^- = Hg(Gly)_2^\circ$	8.9	4

(continued)

TABLE A-7 (continued)

Reaction	Log $\overset{\circ}{K}$	Reference
$Zn^{2+} + OH^- = ZnOH^+$	4.95	4
$Zn^{2+} + 2OH^- = Zn(OH)_2^\circ$	12.89	4
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	14.22	4
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	15.48	4
$Zn^{2+} + Cl^- = ZnCl^+$	- 0.56	4
$Zn^{2+} + SO_4^{2-} = ZnSO_4^\circ$	2.8	4

*Temperature not given.

†Equal sign means reversible reaction.

References: 1 - Bolt and Bruggenwert, 1976
4 - Rubin, 1976

Note: Formation constants apply to temperature = 25°C and pressure = 1 atm.

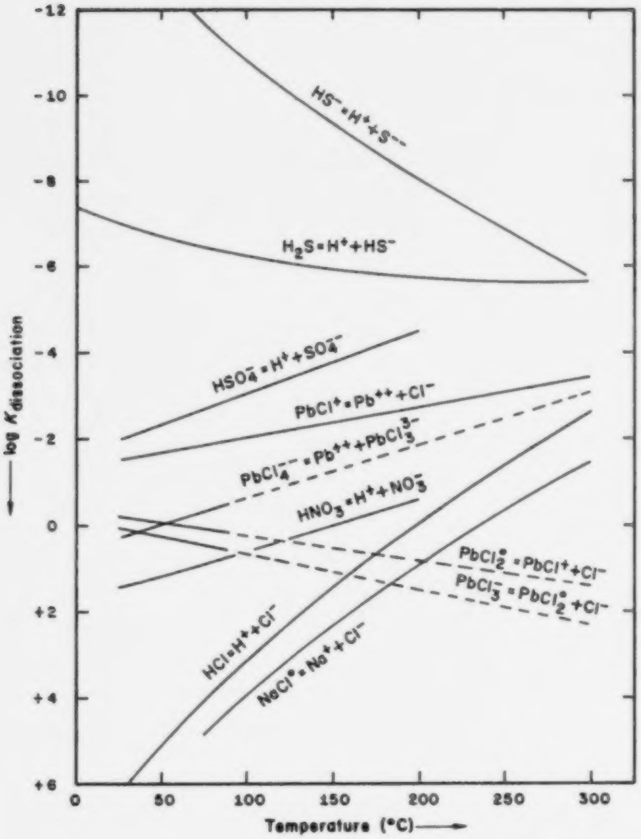


Figure A-2. Dissociation constants of various dissolved species as a function of temperature. Dashed lines indicate extrapolations (after Helgeson, 1964).

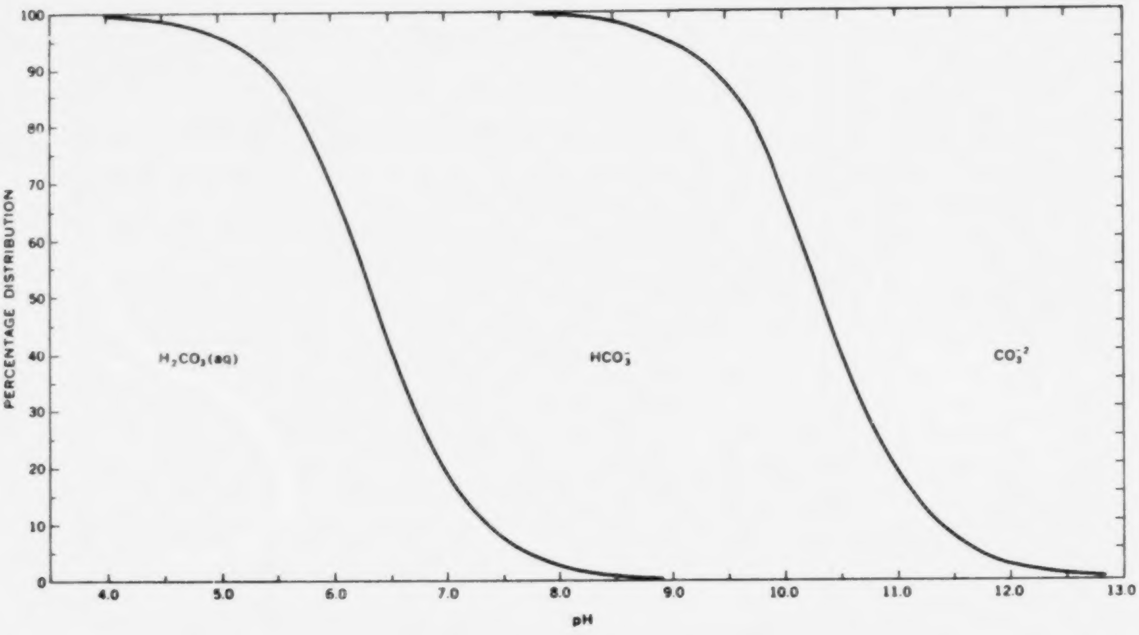


Figure A-3. Percentages of total dissolved carbon dioxide species in solution as a function of pH, 25°C; pressure 1 atmosphere (Hem, 1970).

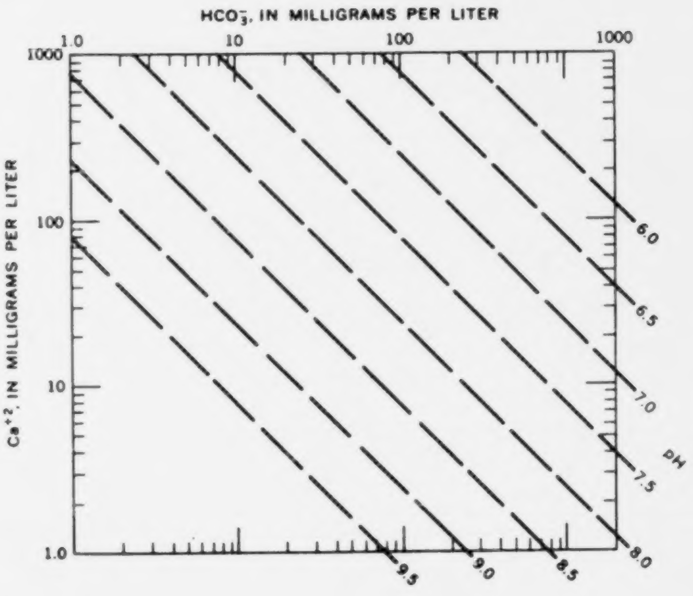
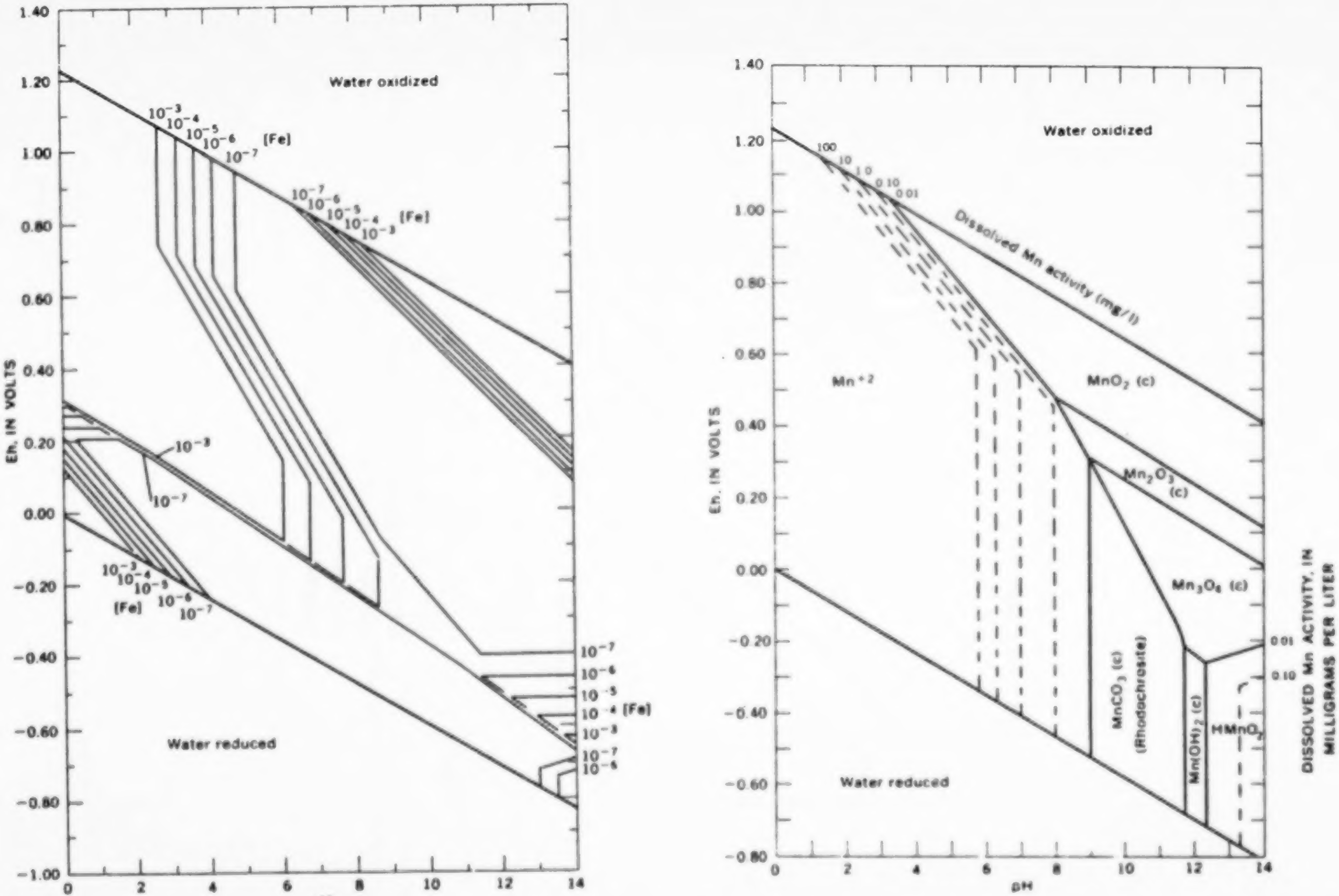


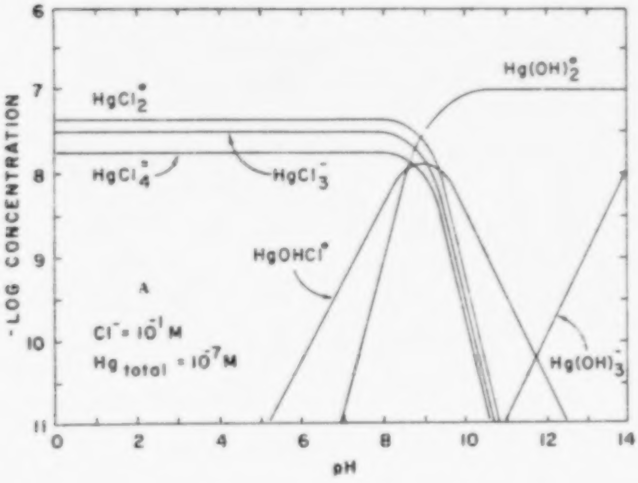
Figure A-4. Equilibrium pH in relation to calcium and bicarbonate activities in solutions in contact with calcite; total pressure 1 atmosphere; temperature 25°C (Hem, 1970).



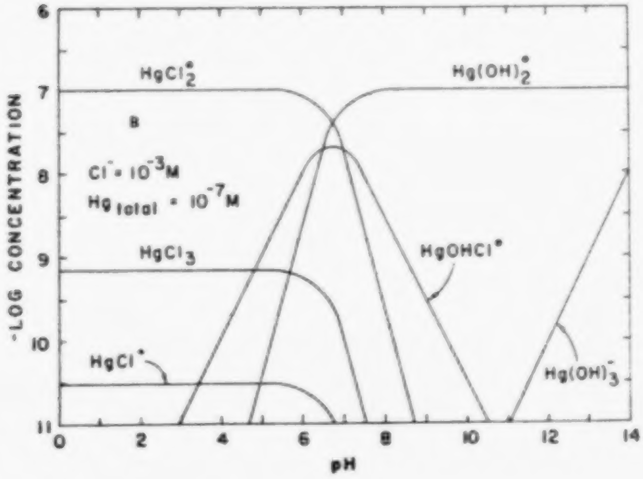
a. - Solubility of iron in moles per liter as function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of sulfur species 96 mg/l as SO_4^{-2}, and carbon dioxide species 61 mg/l as HCO_3^-.

b. - Fields of stability of solids and solubility of manganese as a function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of dissolved carbon dioxide species 100 mg/l as HCO_3^-. Sulfur species absent.

Figure A-5. Examples of Eh - pH diagrams for iron and manganese (Hem, 1970).

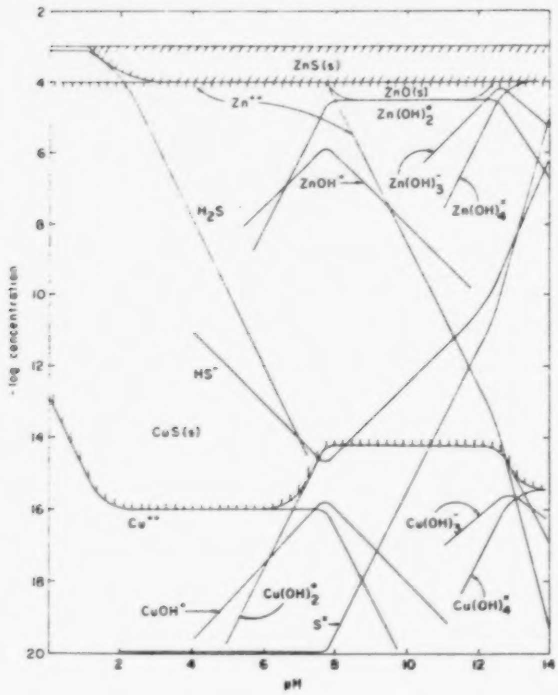


a. Total chloride = 10^{-1}M

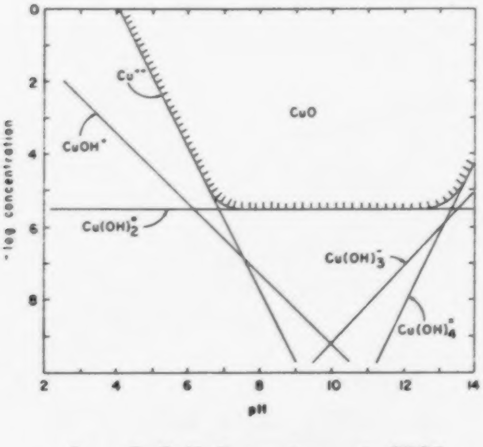


b. Total chloride = 10^{-3}M

Figure A-6. Examples of log concentration-pH diagrams for mercury at 25°C (Rubin, 1976, used with permission of Ann Arbor Science Publishers, Inc.).

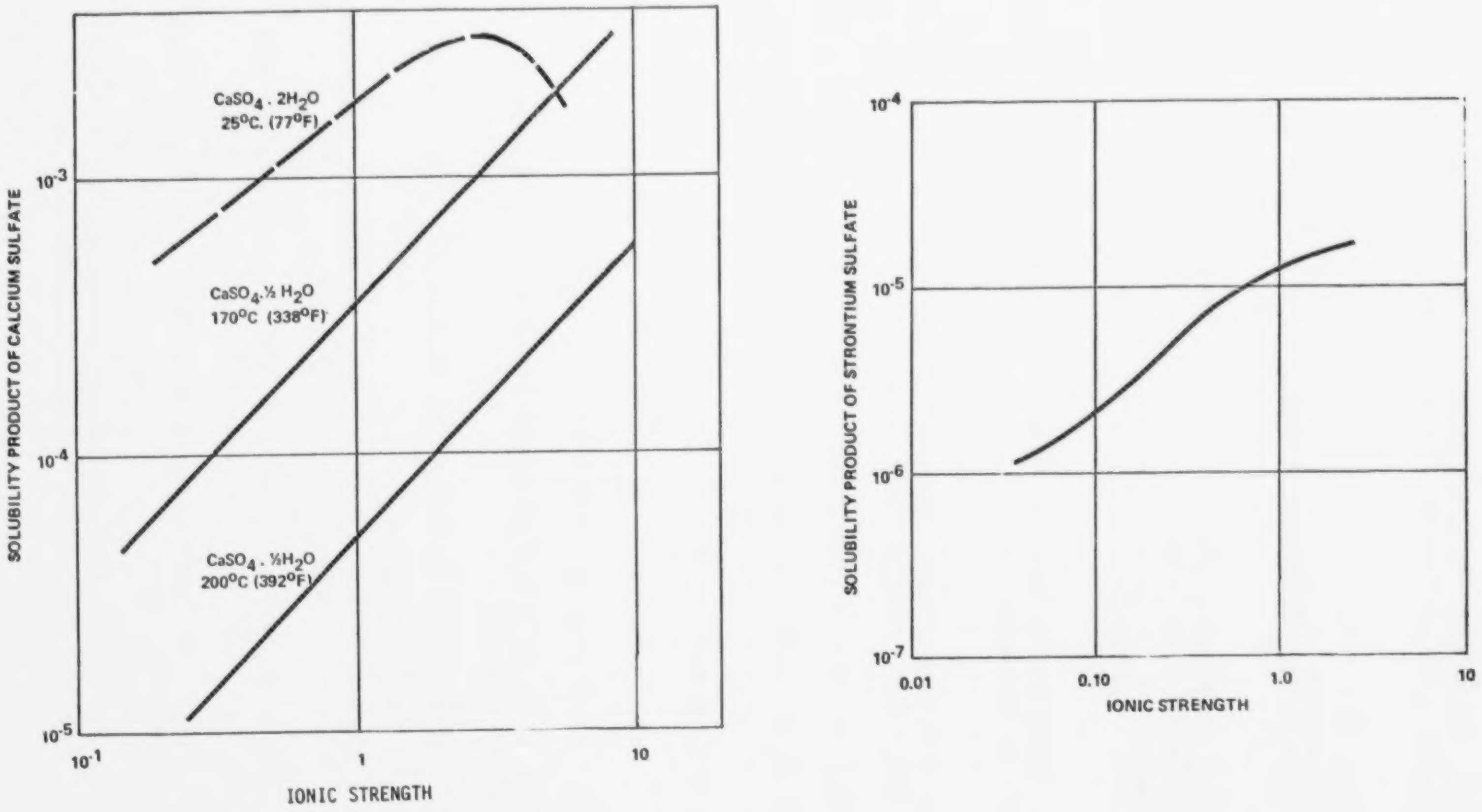


a. Heterogeneous ZnS-Cu(II)-H_2O system at 25°C



b. CuO-H_2O system at 25°C

Figure A-7. Log concentration-pH solubility diagrams for zinc and copper (Rubin, 1976, used with permission of Ann Arbor Science Publishers, Inc.).



a. Solubility of Calcium Sulfate

b. Solubility of Strontium Sulfate at 25°C

Figure A-8. Variation of solubility products for calcium sulfate and strontium sulfate as a function of ionic strength (after Bechtel, 1976).

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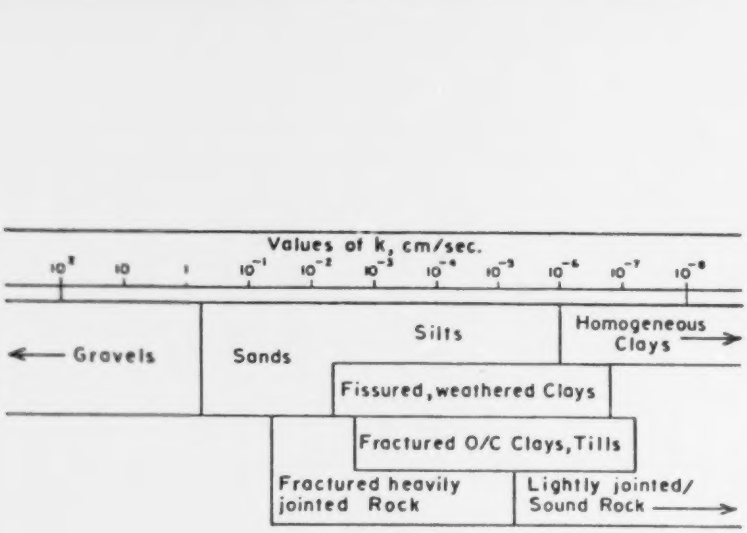
APPENDIX B

SOIL PROPERTIES

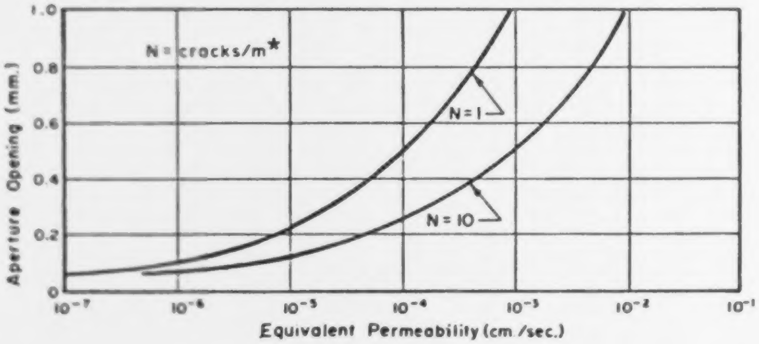
TABLE B-1. PARTICLE SIZE RANGES AND PERMEABILITY FOR SELECTED MATERIALS

		Particle size range				"Effective" size		Permeability coefficient-k				
		Inches		Millimeters								
		$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	D_{20} in.	D_{10} mm.	Ft./yr.	Ft./mo.	Ft./day	Cm./min.	Cm./sec.
Turbulent flow	Derrick STONE	120	36	--	--	48	--	100×10^6	100×10^5	280×10^3	60×10^2	100
	One-man STONE	12	4	--	--	6	--	30×10^6	30×10^5	85×10^3	18×10^2	30
	Clean, fine to coarse GRAVEL	3	1/4	80	10	1/2	--	10×10^6	10×10^5	28×10^3	6×10^2	10
	Fine, uniform GRAVEL	3/8	1/16	8	1.5	1/8	--	5×10^6	5×10^5	14×10^3	3×10^2	5
	Very coarse, clean, uniform SAND	1/8	1/32	3	0.8	1/16	--	3×10^6	3×10^5	8×10^3	1.8×10^2	3
Laminar flow	Uniform, coarse SAND	1/8	1/64	2	0.5	--	0.6	0.4×10^6	0.4×10^5	1×10^3	24	0.4
	Uniform, medium SAND	--	--	0.5	0.25	--	0.3	0.1×10^6	0.1×10^5	0.3×10^3	6	0.1
	Clean, well-graded SAND AND GRAVEL	--	--	10	0.05	--	0.1	0.01×10^6	0.01×10^5	0.03×10^3	0.6	0.01
	Uniform, fine SAND	--	--	0.25	0.05	--	0.06	4000	400	11	0.24	40×10^{-4}
	Well-graded, silty SAND AND GRAVEL	--	--	5	0.01	--	0.02	400	40	1	24×10^{-3}	4×10^{-4}
	Silty SAND	--	--	2	0.005	--	0.01	100	10	280×10^{-3}	6×10^{-3}	10^{-4}
	Uniform SILT	--	--	0.05	0.005	--	0.006	50	5	140×10^{-3}	3×10^{-3}	0.5×10^{-4}
	Sandy CLAY	--	--	1.0	0.001	--	0.002	5	0.5	14×10^{-3}	0.3×10^{-3}	0.05×10^{-4}
	Silty CLAY	--	--	0.05	0.001	--	0.0015	1	0.1	3×10^{-3}	0.06×10^{-3}	0.01×10^{-4}
	CLAY (30 to 50% clay sizes)	--	--	0.05	0.0005	--	0.0003	0.1	0.01	0.3×10^{-3}	0.006×10^{-3}	0.001×10^{-4}
	Colloidal CLAY (-2μ≥50%)	--	--	0.01	10Å	--	40Å	0.001	10^{-4}	3×10^{-6}	6×10^{-8}	10^{-9}

*Adapted from Hough, Soils Engineering. Values listed are approximate.


Values of k, cm/sec.
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Gravels
Sands
Silts
Homogeneous Clays
Fissured, weathered Clays
Fractured O/C Clays, Tills
Fractured heavily jointed Rock
Lightly jointed/ Sound Rock

a. Approximate Range of Permeability in Soil/Rock



*number of cracks intersected by well

b. Equivalent Permeability of a Simple Array of Parallel Cracks

Figure B-1. Graphs for estimating permeability based on gross material characteristics (Milligan, 1976).

TABLE B-2. TECHNIQUES FOR MEASURING PERMEABILITY

a. Direct testing of in situ permeability in soils

Method	Technique	Remarks on application	Method rating	Reference
Ⓐ Augerhole	Shallow uncased hole in unsaturated material above water level	Difficult to maintain water levels in coarse gravels	Poor	USBR (1968)
Test Pit	Square OR rectangular test pit (equivalent to circular hole above)		Poor	Lacroix (1960)
Ⓑ Cased borehole (no inserts)	i) Falling/rising head Δh in casing measured VS time ii) Constant head maintained in casing, outflow, Q VS time	Borehole must be flushed Possible fines clog base (falling Δh) Pumping (rising Δh) where WL lowered excessively	Fair	Hvorslev (1951) USBR (1968)
Ⓒ Cased borehole (inserts used)				
i) Sand filter plug	i) Generally falling head, Δh measured VS time only	Single tests only Cannot be used as boring is advanced	Fair	Hvorslev (1951)
ii) Perforated/slotted casing in lowest section	ii) Variable heads possible			
iii) Well point placed in hole, casing drawn back	iii) As for (ii) above		Fair to good	
Ⓓ Piezometers/Permeameters (with OR without casing)	i) Suction Bellows apparatus (independent of boring) inflow ONLY measured VS time	Restricted to fine sands, coarse silts, variable bellows required 'k' range 10^{-4} to 10^{-7} cm/sec	↑ Good (local zones) ↓	Golder, Gass (1963)
	ii) Short Cell (Cementation) (independent of boring) outflow ONLY measured VS time	Carried out in adit or tunnel		Golder, Gass (1963)
	iii) Piezometer tip pushed into soft deposits/placed in boring, sealed casing withdrawn/pushed ahead of boring Constant head, outflow measured VS time Variable heads also possible	Possible tip 'smear' when pushed. Δu set up in pumping tip Danger of hydraulic fracture		Gibson (1966) Wilkes (1974) Hvorslev (1951) Bjerrum, *et al*. (1972)
Ⓔ Well pumping test	Drawdown in central well monitored in observation wells on at least two 90° radial directions	Screened portion should cover complete stratum tested	Excellent (Mass permeability of foundation material)	Todd (1959)
Ⓕ Test excavation pumping test(s)	Monitoring more extensive than Ⓔ during excavation dewatering (Initial construction stage)	Expensive, but of direct benefit to contractual casing		

Source: Milligan, 1976

(continued)

TABLE B-2. (continued)

b. Direct testing of in situ permeability in rock

Method	Technique	Remarks on application	Method rating	Reference
Ⓐ Borehole (simple tests)	i) Water gain/loss in drilling ii) Simple variable/constant head tests in open boreholes	i) Gives possible indication of pervious zones. Must be supplemented by detailed examination of core. ii) Similar to Table a., Ⓑ (limited value).	Poor	USBR (1968) Dick (1975)
Ⓑ Borehole packer tests	i) Single packer tests (during advance of boring) ii) Double packer tests (in completed boreholes) Pressure tests genetally carried out in BH's (AX to NX size)	Expanding leather/rubber packers may provide inadequate seal. Pneumatic packers superior to other types, but limited to pressures < 200 lb/sq.in.	i) Fair ii) Poor to fair	USBR (1968) Sherard, *et al*. (1963) Sharp (1970) Dick (1975)
Ⓒ Permeameters/inserts	Variable head tests in: i) Sealed individual piezometers (local zone) ii) Continuous borehole piezometers	i) Similar to Table a, Ⓓ - local zones tested. Limited application. ii) Possible to monitor water pressure variation over complete boring to 200m depth. Needs interpretation to assess 'k'.	i) Fair to good (local zone) ii) Fair (Potential good)	i) USBR (1968) ii) Londe (1973)
Ⓓ Well pumping test	Normally carried out in open central well. Observation wells at radii, 90°.	Similar to Table a, Ⓔ. Screen/perforated casing often NOT required.	Excellent (Mass permeability)	

Source: Milligan, 1976

(continued)

TABLE B-2. (continued)

c. Indirect assessment of in situ permeability in soils (rock)

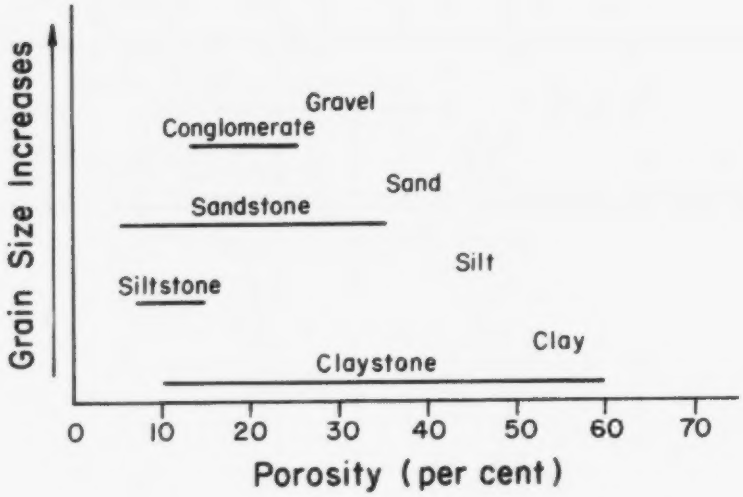
Method	Technique	Remarks on application	Method rating	Reference
Ⓐ **Tests on samples (Inc. natural exposures)**	i) Gradation ii) Inspection, macro-structure iii) Laboratory 'k'	i) D_{10}^2 applicable to uniform sands ii) Useful in qualitative sense iii) Often inapplicable to field conditions	Fair (to good?) Poor	Loudon (1952) Golder, Gass (1963) Rowe (1972)
Ⓑ **Geophysical (Electric well logging)**	i) Multi-electrode resistivity ii) Single point resistance potential iii) Fluid conductivity, temperature	Continuous profiling of borings can be carried out at low cost (Requires further correlation with in situ direct testing)	Fair Future development good	Guyod (1966) Robinson (1974)
Ⓒ **Observations of natural OR induced seepage**	**Measurement and analysis of data from:** i) Observation wells ii) Piezometers iii) Dyes, tracers, radioactive isotopes	Provides the best form of assessing permeabilities, in situ, in relation to engineering problems, in soil OR rock	Excellent	Walker (1955) Terzaghi (1960)(1964) Golder, Gass (1963) Sharp (1970) Todd (1959)

Source: Milligan, 1976

TABLE B-3. MEAN VALUES OF FIELD CAPACITY, PERMANENT WILTING PERCENTAGE AND AVAILABLE WATER FOR SOME SOIL TEXTURAL CLASSES

	Fractions of soil volume		
Soil type	Field capacity	Permanent wilting	Available water
Sand	0.09	0.02	0.07
Sandy loam	0.27	0.11	0.16
Loam	0.34	0.13	0.21
Silt loam	0.38	0.14	0.24
Clay loam	0.30	0.16	0.14
Clay	0.39	0.22	0.17
Peat	0.55	0.25	0.30

Source: Salter and Williams (1965) as presented in Monteith, 1975



Note: Value for siltstone is displaced to the left, probably because siltstone measurements were based on very few samples

Figure B-2. Common range of porosity in typical sediments and sedimentary rocks (after Longwell et al., 1969).

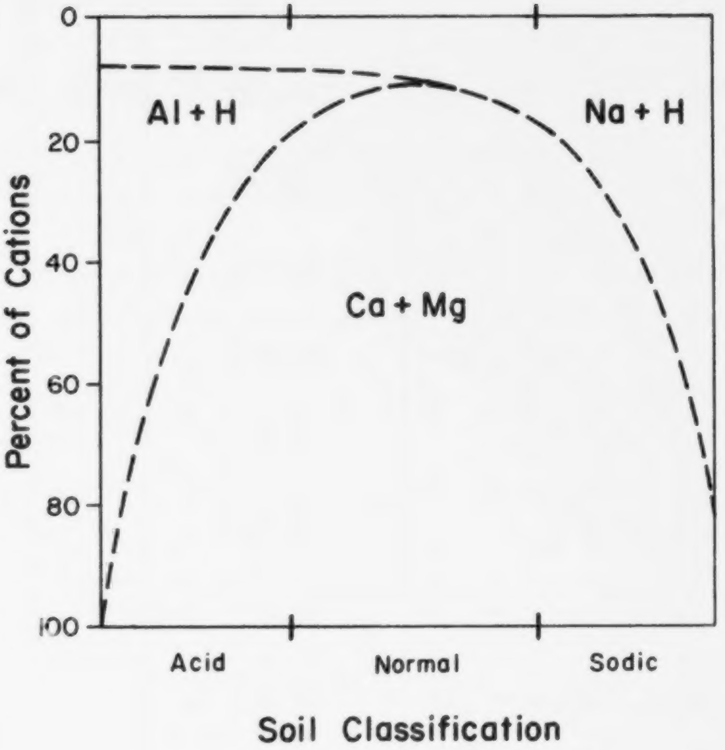


Figure B-3. Schematic presentation of the cationic composition of soils (after Bolt and Bruggenwert, 1976).

TABLE B-4. CATION EXCHANGE CAPACITY FOR SOME SOIL COMPONENTS

Component	Ca CEC,* meq/100g	K CEC,** meq/100g
Micas	6-140	3-6
Vermiculites	140-180	2-7
Smectites	80-140	80-140
Amorphous minerals	20-160	20-160
Humus	200-300	200-300
Kaolinite	3-15	
Halloysite ($2H_2O$)	5-10	
Halloysite ($4H_2O$)	40-50	
"Illites" (hydrous micas)	10-40	
Chlorite	10-40?	
Glauconite	11-30	
Glauconite	30	

*CA CEC = cation exchange capacity as measured by exchanging calcium ions.

**K CEC = cation exchange capacity as measured by exchanging potassium ions.

Source: Data from Jackson, 1971; Garrels and Christ, 1965; and Bolt and Bruggenwert, 1976

TABLE B-5. CATION EXCHANGE CAPACITIES FOR SELECTED SOILS

Soil type	$CaCO_3$ (wt.%)	Clay (%)	Humus (%)	CEC (meq/100g)	Cationic composition (% of CEC)				
					H/Al	Ca	Mg	K	Na
Holland, recent marine clay (periodically submerged)	0.3	29.3	23.3	60.7	0	26.2	32.8	6.9	34.1
Holland, young seaclay soil	5.2	48.9	3.0	18.5	0	81.8	10.8	6.5	0.9
Holland, young lake deposit (IJsselmeerpolders)	10.1	19.9	2.7	36.5	0	90.3	7.5	2.0	0.2
Holland, river basin soil	1.3	40.3	5.3	78.1	0	90.6	8.5	0.6	0.3
Surinam, acid sulphate soil (reclaimed coastal plain)	0	52.0	4.3	38.0	20	39	27	3	0.5
U.S.A., gray brown podsolic (alfisol)	0	12.8	1.2	13.1	33.6	51.1	12.2	3.1	0.0
Holland, humus podsol (spodosol)	0	2	4.2	8.8	53.7	35.6	6.0	3.3	1.4
Puerto Rico, Latosol (oxisol)	0	50.3	7.4	30.4	94.9	1.6	2.6	0.3	0.6
U.S.A., reddish brown lateritic soil (ultisol)	0	42.0	7.7	50.6	56.9	28.6	9.3	5.0	0.2
Rumenia, chernozem (mollisol)	0.2	39.5	2.6	33.9	10.2	66.1	19.6	1.8	2.3
U.S.A., self-mulching clay soil (vertisol)	2	43.0	1.3	50.8	2.2	78.3	16.2	3.1	0.2
U.S.A., saline soil	8	?	?	25.6	0	67	22	3	8
Turkey, saline alkali soil	5	?	?	10.4	0	27	24	2	47
India, saline alkali soil	2	20.0	?	9.0	0	2	1	2	95
Turkey, alkali soil	0	?	?	11.2	0	30	29	2	39
Rumenia, solodized solonetz	0	27.4	2.4	19.7	17.9	25.9	25.4	1.4	29.4

after Bolt and Bruggenwert, 1976

TABLE B-6. SPECIFIC SURFACE AREAS

Mineral	Particle diameter	Specific surface area
Coarse sand	1.0 mm	0.0026 m^2/g
Medium clay	0.001 mm	2.26 m^2/g
Fine clay	0.0005 mm	433 m^2/g
Na-illite		50-200 m^2/g
Na-montmorillonite		600-800 m^2/g

Source: Gherini, 1975

APPENDIX C

ADSORPTION COEFFICIENTS

ION EXCHANGE COEFFICIENTS

Preferences for ion exchange or adsorption of selected cations or ions can be expressed by the following equations (Bolt and Bruggenwert, 1976):

For ions of equal valence,

$$\frac{\overset{+}{\gamma}_a}{\overset{+}{\gamma}_b} = K_{a/b} \frac{C_{o,a}}{C_{o,b}} \qquad (1)$$

where $K_{a/b}$ = Kerr selectivity coefficient

$\overset{+}{\gamma}_a$ = amount of ion "a" on (bound to) the soil solid phase, meq/100 grams soil

$\overset{+}{\gamma}_b$ = amount of ion "b" on (bound to) the soil solid phase, meq/100 grams soil

$C_{o,a}$ = concentration of ion "a" in soil solution, meq/kg solution

$C_{o,b}$ = concentration of ion "b" in soil solution, meq/kg solution

$K_{a/b}$ can be shown to be related

$$K_{D_b} = \frac{1}{K_{a/b}} \frac{m_o}{C_o}$$

where m_o = cation exchange capacity of solid medium, meq/g

C_o = initial solution concentration ([a] + [b]), meq/ml

For monovalent/divalent ion preference

$$\frac{\overset{+}{Y}_{+}}{\overset{+}{Y}_{2+}} = \frac{K_G \, C_{o,1+}}{\sqrt{\frac{C_{o,2+}}{2}}} \qquad (2)$$

where $\overset{+}{Y}_{+}$ = amount of monovalent cation on (bound to) the soil solid phase, meq/100 g soil

$\overset{+}{Y}_{2+}$ = amount of divalent cation on (bound to) the soil solid phase, meq/100 g soil

K_G = Gapon exchange constant

$C_{o,1+}$ = concentration of monovalent cation in soil solution, meq/kg solution

$C_{o,2+}$ = concentration of divalent cation in soil solution, meq/kg solution

Values of the Kerr selectivity coefficients for several ion pairs are given below:

$K_{K/Na}$	5	$K_{Ca/Ba}$	~ 1
$K_{NH_4/Na}$	~ 5	$K_{Ca/Sr}$	~ 1
$K_{NH_4/Rb}$	~ 5	$K_{Ca/Zn}$	~ 1
$K_{H/K}$	~ 1	$K_{Ca/Co}$	~ 1
$K_{Ca/Mg}$	1.2	$K_{Ca/Cu}$	~ 1
$K_{Ca/Ni}$	~ 1		

Values of the Gapon exchange coefficient for several ion pairs are listed below:

$K_{G_{Na/Ca}}$ = ½ (moles/liter)$^{-½}$ if concentration of ions was given in moles/liter

$K_{G_{Na/Ca}}$ = 1 (moles/liter)$^{-½}$ in montmorillonitic soils

$K_{G_{K/Na}}$ = ½ (C_K + C_{Na}) if concentration of sodium (C_{Na}) is much greater than potassium (C_K)

The Gapon exchange constant for two divalent cations where the Kerr selectivity coefficient is approximately 1 can be estimated as the sum of the concentrations of the two ions.

THE DISTRIBUTION COEFFICIENT, K_D

Definition

This coefficient is used in the mass transport equations to account for pollutant removal from solution due to "sorption" on the soil or rock. K_D is defined for specific pollutants by the following ratio:

$$K_D = \frac{\text{concentration of pollutant sorbed on soil/rock, mg of pollutant per gram of solid}}{\text{Concentration of pollutant in solution, mg of pollutant per milliliter of solution}}$$

The distribution coefficient is an equilibrium constant. As such its use requires that equilibrium conditions be maintained between the distribution of pollutant in solution and on the solid phase. Equilibrium is more closely approached in slow moving ground waters than in rapidly flowing surface water systems (e.g., compare river velocities of about 1 ft/sec to seepage velocities of ground water of about 1 ft/day).

The major processes creating the observed distributions of pollutants between solid and liquid phases include adsorption, absorption, and ion-exchange.

K_D in Relation to Pollutant Migration

The ratio of the ground water seepage velocity, V_s, to the pollutant migration velocity, V_p, is given by

$$\frac{V_s}{V_p} = 1 + \frac{K_D \rho}{\rho}$$

where K_D = the distribution coefficient, defined above [mℓ/g]

ρ = the in situ bulk density of the permeable media: weight of solids per unit volume of soil or rock as packed [g/mℓ]

ε = void fraction = ground water volume/volume of solid

For a given pollutant, a K_D value of zero would indicate that the pollutant behaves conservatively. K_D values for tritium, chloride, and nitrate in many systems approach zero. A high K_D value indicates that the pollutant sorbs strongly on the soil/rock matrix; its migration velocity would be much lower than the liquid seepage velocity.

Dependencies of the Distribution Coefficient

K_D values depend upon several factors. Listed below are those factors which most strongly influence K_D values:

- Chemical form (species) of the pollutant of concern
- Mineralogical and physical characteristics of the solid phase
- Surface coating on the solid phase (e.g., amorphous iron hydroxide coatings)
- Concentrations of other constituents in solution (e.g., hydrogen ions, complexing agents, ions which form insoluble compounds with the pollutant of concern)
- Redox state of the system

The various forms in which a pollutant can exist (e.g., for sulfur, H_2S, HS^-, SO_4^{2-}, R-SH, etc.) can be expected to exhibit differing migration behavior.

Although K_D values have been largely developed based upon the mass of the solid phase present, the use of soil-specific surface areas is a better, but more expensive, technical approach. The behavior of certain aqueous pollutants (e.g., inorganic mercury) has been shown to be correlated most strongly with the amount of surface area present. For mercury the mineralogical type of surface is far less important.

It should be noted that because of the above dependencies, and the common lack of documentation of such during experimental determination of K_D values, actual values are typically site-specific.

K_D Values

A considerable amount of work has been done to determine K_D values for radionuclides associated with the nuclear power industry. Values for other pollutant species are limited. Data can sometimes be obtained from the soil science literature for species of agricultural interest by analysis of experimentally determined Langmuir and Freundlich isotherms.

The Langmuir adsorption equation is commonly presented as follows (Adamson, 1967):

$$\frac{x}{m} = \frac{kb\ C_o}{1 + kC_o}$$

where $\frac{x}{m}$ = amount of pollutant adsorbed per unit weight of absorbent

C_o = equilibrium concentration of the adsorbing compound in solution

k = constant (relates to bonding energies)

b = maximum amount of pollutant adsorbable

At the low concentrations which are common for many ground water pollutants kC_o is small relative to 1 and the above equation reduces to

$$\frac{x}{m} \cong kb\, C_o \cong K_D\, C_o$$

K_D can thus be approximated by the slope of the Langmuir adsorption isotherm in the linear region. (A similar demonstration can be made using the Freundlich equation with $n = 1$.)

K_D values are usually determined by batch experiments where a given amount of soil is added to a solution of known pollutant concentration and chemical composition. The resulting mix is agitated until the pollutant concentration in solution no longer decreases (equilibrium condition).

Field determination of K_D values is also possible. This requires the use of non-soil-interactive tracers such as tritium and typically is more expensive than laboratory batch experiments. A pertinent discussion of K_D measurement techniques is given in the EPA report 520/6-78-007, Vol. 1, 1978, "Radionuclide Interactions with Soil and Rock Media."

Specific values of K_D for inorganic mercury, inorganic copper, boron, and tritium are presented in Table C-1.

TABLE C-1. EXAMPLE DISTRIBUTION COEFFICIENTS FOR SELECTED SPECIES AND SYSTEM CHARACTERISTICS

Species	Conditions	K_D, value, mℓ/gram
Hg_T (total inorganic mercury; includes Hg complexed with OH^-, and Cl^-)	$[Cl^-] = 10^{-3}$ molar pH = 7 Hg @ trace concentrations T = 20°C Soil = silt, sp. surf area = 1 m^2/g	$2.6 \times 10^6 \frac{ml}{gm}$ (1)
Cu_T (total inorganic copper; complexed with inorganic SW anions)	$[Cl^-] \cong 0.5$ pH ≅ 8 Cu @ trace concentrations	1,000 to 45,000 $\frac{ml}{gm}$ (2)
B (fully protonated orthoboric acid H_3BO_3; common form of boron in natural waters)	EC = 0.6 mmhos (25°C) pH ≅ 6.6 T = 30°C (solid phase: Terra rossa soil gp.) $[B] \leq 35$ ppm	9 ml/gm (3)
^3H (tritiated water)	Sandy soils clays and other hydrated minerals	0 ml/gm (4) ∿0 ml/gm

Source:

(1) Gherini, S., 1975
(2) Emerson, R.R. and F.L. Harrison, 1978
(3) Hadas, A. and J. Hagin, 1971
(4) Ames, 1978

APPENDIX D

MATHEMATICAL FUNCTIONS

TABLE D-1. TABLES OF ERROR AND ASSOCIATED FUNCTIONS (after Crank, 1976)

	Error Functions of X				
x	e^{x^2} erfc x	$4\pi^{-\frac{1}{2}} x e^{-x^2}$	$2\pi^{-\frac{1}{2}} e^{-x^2}$	erf x	erfc x
0	1·0	0	1·1284	0	1·0
0·05	0·9460	0·1126	1·1256	0·056372	0·943628
0·1	0·8965	0·2234	1·1172	0·112463	0·887537
0·15	0·8509	0·3310	1·1033	0·167996	0·832004
0·2	0·8090	0·4336	1·0841	0·222703	0·777297
0·25	0·7703	0·5300	1·0600	0·276326	0·723674
0·3	0·7346	0·6188	1·0313	0·328627	0·671373
0·35	0·7015	0·6988	0·9983	0·379382	0·620618
0·4	0·6708	0·7692	0·9615	0·428392	0·571608
0·45	0·6423	0·8294	0·9215	0·475482	0·524518
0·5	0·6157	0·8788	0·8788	0·520500	0·479500
0·55	0·5909	0·9172	0·8338	0·563323	0·436677
0·6	0·5678	0·9447	0·7872	0·603856	0·396144
0·65	0·5462	0·9614	0·7395	0·642029	0·357971
0·7	0·5259	0·9678	0·6913	0·677801	0·322199
0·75	0·5069	0·9644	0·6429	0·711156	0·288844
0·8	0·4891	0·9520	0·5950	0·742101	0·257899
0·85	0·4723	0·9314	0·5479	0·770668	0·229332
0·9	0·4565	0·9035	0·5020	0·796908	0·203092
0·95	0·4416	0·8695	0·4576	0·820891	0·179109
1·0	0·4276	0·8302	0·4151	0·842701	0·157299
1·1	0·4017	0·7403	0·3365	0·880205	0·119795
1·2	0·3785	0·6416	0·2673	0·910314	0·089686
1·3	0·3576	0·5413	0·2082	0·934008	0·065992
1·4	0·3387	0·4450	0·1589	0·952285	0·047715
1·5	0·3216	0·3568	0·1189	0·966105	0·033895
1·6	0·3060	0·2791	0·0872	0·976348	0·023652
1·7	0·2917	0·2132	0·0627	0·983790	0·016210
1·8	0·2786	0·1591	0·0442	0·989091	0·010909
1·9	0·2665	0·1160	0·0305	0·992790	0·007210
2·0	0·2554	0·0827	0·0207	0·995322	0·004678
2·1	0·2451	0·0576	0·0137	0·997021	0·002979
2·2	0·2356	0·0393	0·0089	0·998137	0·001863
2·3	0·2267	0·0262	0·0057	0·998857	0·001143
2·4	0·2185	0·0171	0·0036	0·999311	0·000689
2·5	0·2108	0·0109	0·0022	0·999593	0·000407
2·6	0·2036	0·0068	0·0013	0·999764	0·000236
2·7	0·1969	0·0042	0·0008	0·999866	0·000134
2·8	0·1905	0·0025	0·0004	0·999925	0·000075
2·9	0·1846	0·0015	0·0003	0·999959	0·000041
3·0	0·1790	0·0008	0·0001	0·999978	0·000022

Note: erfc(x) = 1 -erf(x)
erf(-x) = -erf(x)

TABLE D-2. NORMAL CURVE OF ERROR (Hodgman *et al*., 1961)

x	Area	Ordinate $\phi(x)$	Second derivative $\phi''(x)$	Third derivative $\phi'''(x)$	Fourth derivative $\phi^{iv}(x)$	*x*	Area	Ordinate $\phi(x)$	Second derivative $\phi''(x)$	Third derivative $\phi'''(x)$	Fourth derivative $\phi^{iv}(x)$	*x*	Area	Ordinate $\phi(x)$	Second derivative $\phi''(x)$	Third derivative $\phi'''(x)$	Fourth derivative $\phi^{iv}(x)$	*x*	Area	Ordinate $\phi(x)$	Second derivative $\phi''(x)$	Third derivative $\phi'''(x)$	Fourth derivative $\phi^{iv}(x)$
.00	.0000	.3989	−.3989	.0000	1.1968	.50	.1915	.3521	−.2641	.4841	.5501	1.00	.3413	.2420	.0000	.4839	−.4839	1.50	.4332	.1295	.1619	.1457	−.7043
.01	.0040	.3989	−.3989	.0120	1.1965	.51	.1950	.3503	−.2592	.4895	.5279	1.01	.3438	.2396	.0048	.4790	−.4983	1.51	.4345	.1276	.1633	.1387	−.6994
.02	.0080	.3989	−.3987	.0239	1.1956	.52	.1985	.3485	−.2543	.4947	.5056	1.02	.3461	.2371	.0096	.4740	−.5122	1.52	.4357	.1257	.1647	.1317	−.6942
.03	.0120	.3988	−.3984	.0359	1.1941	.53	.2019	.3467	−.2493	.4996	.4831	1.03	.3485	.2347	.0143	.4688	−.5257	1.53	.4370	.1238	.1660	.1248	−.6888
.04	.0160	.3986	−.3980	.0478	1.1920	.54	.2054	.3448	−.2443	.5043	.4605	1.04	.3508	.2323	.0190	.4635	−.5389	1.54	.4382	.1219	.1672	.1180	−.6831
.05	.0199	.3984	−.3974	.0597	1.1894	.55	.2088	.3429	−.2392	.5088	.4378	1.05	.3531	.2299	.0236	.4580	−.5516	1.55	.4394	.1200	.1683	.1111	−.6772
.06	.0239	.3982	−.3968	.0716	1.1861	.56	.2123	.3411	−.2341	.5131	.4150	1.06	.3554	.2275	.0281	.4524	−.5639	1.56	.4406	.1182	.1694	.1044	−.6710
.07	.0279	.3980	−.3960	.0834	1.1822	.57	.2157	.3391	−.2289	.5171	.3921	1.07	.3577	.2251	.0326	.4467	−.5758	1.57	.4418	.1163	.1704	.0977	−.6646
.08	.0319	.3977	−.3951	.0952	1.1778	.58	.2190	.3372	−.2238	.5209	.3691	1.08	.3599	.2227	.0371	.4409	−.5873	1.58	.4430	.1145	.1714	.0911	−.6580
.09	.0359	.3973	−.3941	.1070	1.1727	.59	.2224	.3352	−.2185	.5245	.3461	1.09	.3621	.2203	.0414	.4350	−.5984	1.59	.4441	.1127	.1722	.0846	−.6511
.10	.0398	.3970	−.3930	.1187	1.1671	.60	.2258	.3332	−.2133	.5278	.3231	1.10	.3643	.2179	.0458	.4290	−.6091	1.60	.4452	.1109	.1730	.0781	−.6441
.11	.0438	.3965	−.3917	.1303	1.1609	.61	.2291	.3312	−.2080	.5309	.3000	1.11	.3665	.2155	.0500	.4228	−.6193	1.61	.4463	.1092	.1738	.0717	−.6368
.12	.0478	.3961	−.3904	.1419	1.1541	.62	.2324	.3292	−.2027	.5338	.2770	1.12	.3686	.2131	.0542	.4166	−.6292	1.62	.4474	.1074	.1745	.0654	−.6293
.13	.0517	.3956	−.3889	.1534	1.1468	.63	.2357	.3271	−.1973	.5365	.2539	1.13	.3708	.2107	.0583	.4102	−.6386	1.63	.4485	.1057	.1751	.0591	−.6216
.14	.0557	.3951	−.3873	.1648	1.1389	.64	.2389	.3251	−.1919	.5389	.2309	1.14	.3729	.2083	.0624	.4038	−.6476	1.64	.4495	.1040	.1757	.0529	−.6138
.15	.0596	.3945	−.3856	.1762	1.1304	.65	.2422	.3230	−.1865	.5411	.2078	1.15	.3749	.2059	.0664	.3973	−.6561	1.65	.4505	.1023	.1762	.0468	−.6057
.16	.0636	.3939	−.3838	.1874	1.1214	.66	.2454	.3209	−.1811	.5431	.1849	1.16	.3770	.2036	.0704	.3907	−.6643	1.66	.4515	.1006	.1766	.0408	−.5976
.17	.0675	.3932	−.3819	.1986	1.1118	.67	.2486	.3187	−.1757	.5448	.1620	1.17	.3790	.2012	.0742	.3840	−.6720	1.67	.4525	.0989	.1770	.0349	−.5891
.18	.0714	.3925	−.3798	.2097	1.1017	.68	.2517	.3166	−.1702	.5463	.1391	1.18	.3810	.1989	.0780	.3772	−.6793	1.68	.4535	.0973	.1773	.0290	−.5808
.19	.0754	.3918	−.3777	.2206	1.0911	.69	.2549	.3144	−.1647	.5476	.1164	1.19	.3830	.1965	.0818	.3704	−.6861	1.69	.4545	.0957	.1776	.0233	−.5720
.20	.0793	.3910	−.3754	.2315	1.0799	.70	.2580	.3123	−.1593	.5486	.0937	1.20	.3849	.1942	.0854	.3635	−.6926	1.70	.4554	.0941	.1778	.0176	−.5632
.21	.0832	.3902	−.3730	.2422	1.0682	.71	.2612	.3101	−.1538	.5495	.0712	1.21	.3869	.1919	.0890	.3566	−.6986	1.71	.4564	.0925	.1779	.0120	−.5542
.22	.0871	.3894	−.3706	.2529	1.0560	.72	.2642	.3079	−.1483	.5501	.0487	1.22	.3888	.1895	.0926	.3496	−.7042	1.72	.4573	.0909	.1780	.0065	−.5452
.23	.0910	.3885	−.3680	.2634	1.0434	.73	.2673	.3056	−.1428	.5504	.0265	1.23	.3907	.1872	.0960	.3425	−.7094	1.73	.4582	.0893	.1780	.0011	−.5360
.24	.0948	.3876	−.3653	.2737	1.0302	.74	.2704	.3034	−.1373	.5506	.0043	1.24	.3925	.1849	.0994	.3354	−.7141	1.74	.4591	.0878	.1780	−.0042	−.5267
.25	.0987	.3867	−.3625	.2840	1.0165	.75	.2734	.3011	−.1318	.5505	−.0176	1.25	.3944	.1827	.1027	.3282	−.7185	1.75	.4599	.0863	.1780	−.0094	−.5173
.26	.1026	.3857	−.3596	.2941	1.0024	.76	.2764	.2989	−.1262	.5502	−.0394	1.26	.3962	.1804	.1060	.3210	−.7224	1.76	.4608	.0848	.1778	−.0146	−.5079
.27	.1064	.3847	−.3566	.3040	0.9878	.77	.2794	.2966	−.1207	.5497	−.0611	1.27	.3980	.1781	.1092	.3138	−.7259	1.77	.4616	.0833	.1777	−.0196	−.4983
.28	.1103	.3836	−.3535	.3138	0.9727	.78	.2823	.2943	−.1153	.5490	−.0825	1.28	.3997	.1758	.1123	.3065	−.7291	1.78	.4625	.0818	.1774	−.0245	−.4887
.29	.1141	.3825	−.3504	.3236	0.9572	.79	.2852	.2920	−.1098	.5481	−.1037	1.29	.4015	.1736	.1153	.2992	−.7318	1.79	.4633	.0804	.1772	−.0294	−.4789
.30	.1179	.3814	−.3471	.3330	0.9413	.80	.2881	.2897	−.1043	.5469	−.1247	1.30	.4032	.1714	.1182	.2918	−.7341	1.80	.4641	.0790	.1769	−.0341	−.4692
.31	.1217	.3802	−.3437	.3423	0.9250	.81	.2910	.2874	−.0988	.5456	−.1455	1.31	.4049	.1691	.1211	.2845	−.7361	1.81	.4649	.0775	.1765	−.0388	−.4593
.32	.1255	.3790	−.3402	.3515	0.9082	.82	.2939	.2850	−.0934	.5440	−.1660	1.32	.4066	.1669	.1239	.2771	−.7376	1.82	.4656	.0761	.1761	−.0433	−.4494
.33	.1293	.3778	−.3367	.3605	0.8910	.83	.2967	.2827	−.0880	.5423	−.1862	1.33	.4082	.1647	.1267	.2697	−.7388	1.83	.4664	.0748	.1756	−.0477	−.4395
.34	.1331	.3765	−.3330	.3693	0.8735	.84	.2995	.2803	−.0825	.5403	−.2063	1.34	.4099	.1626	.1293	.2624	−.7395	1.84	.4671	.0734	.1751	−.0521	−.4295
.35	.1368	.3752	−.3293	.3779	0.8556	.85	.3023	.2780	−.0771	.5381	−.2260	1.35	.4115	.1604	.1319	.2550	−.7399	1.85	.4678	.0721	.1746	−.0563	−.4195
.36	.1406	.3739	−.3255	.3864	0.8373	.86	.3051	.2756	−.0718	.5358	−.2455	1.36	.4131	.1582	.1344	.2476	−.7400	1.86	.4686	.0707	.1740	−.0605	−.4095
.37	.1443	.3726	−.3216	.3947	0.8186	.87	.3078	.2732	−.0664	.5332	−.2646	1.37	.4147	.1561	.1369	.2402	−.7396	1.87	.4693	.0694	.1734	−.0645	−.3995
.38	.1480	.3712	−.3176	.4028	0.7996	.88	.3106	.2709	−.0611	.5305	−.2835	1.38	.4162	.1540	.1392	.2328	−.7389	1.88	.4700	.0681	.1727	−.0685	−.3894
.39	.1517	.3697	−.3135	.4107	0.7803	.89	.3133	.2685	−.0558	.5276	−.3021	1.39	.4177	.1518	.1415	.2254	−.7378	1.89	.4706	.0669	.1720	−.0723	−.3793
.40	.1554	.3683	−.3094	.4184	0.7607	.90	.3159	.2661	−.0506	.5245	−.3203	1.40	.4192	.1497	.1437	.2180	−.7364	1.90	.4713	.0656	.1713	−.0761	−.3693
.41	.1591	.3668	−.3051	.4259	0.7408	.91	.3186	.2637	−.0453	.5212	−.3383	1.41	.4207	.1476	.1459	.2107	−.7347	1.91	.4719	.0644	.1705	−.0797	−.3592
.42	.1628	.3653	−.3008	.4332	0.7206	.92	.3212	.2613	−.0401	.5177	−.3559	1.42	.4222	.1456	.1480	.2033	−.7326	1.92	.4726	.0632	.1697	−.0832	−.3492
.43	.1664	.3637	−.2965	.4403	0.7001	.93	.3238	.2589	−.0350	.5140	−.3731	1.43	.4236	.1435	.1500	.1960	−.7301	1.93	.4732	.0620	.1688	−.0867	−.3392
.44	.1700	.3621	−.2920	.4472	0.6793	.94	.3264	.2565	−.0299	.5102	−.3901	1.44	.4251	.1415	.1519	.1887	−.7274	1.94	.4738	.0608	.1679	−.0900	−.3292
.45	.1736	.3605	−.2875	.4539	0.6583	.95	.3289	.2541	−.0248	.5062	−.4066	1.45	.4265	.1394	.1537	.1815	−.7243	1.95	.4744	.0596	.1670	−.0933	−.3192
.46	.1772	.3589	−.2830	.4603	0.6371	.96	.3315	.2516	−.0197	.5021	−.4228	1.46	.4279	.1374	.1555	.1742	−.7209	1.96	.4750	.0584	.1661	−.0964	−.3093
.47	.1808	.3572	−.2783	.4666	0.6156	.97	.3340	.2492	−.0147	.4978	−.4387	1.47	.4292	.1354	.1572	.1670	−.7172	1.97	.4756	.0573	.1651	−.0994	−.2994
.48	.1844	.3555	−.2736	.4727	0.5940	.98	.3365	.2468	−.0098	.4933	−.4541	1.48	.4306	.1334	.1588	.1599	−.7132	1.98	.4762	.0562	.1641	−.1023	−.2895
.49	.1879	.3538	−.2689	.4785	0.5721	.99	.3389	.2444	−.0049	.4887	−.4692	1.49	.4319	.1315	.1604	.1528	−.7089	1.99	.4767	.0551	.1630	−.1052	−.2797
.50	.1915	.3521	−.2641	.4841	0.5501	1.00	.3413	.2420	.0000	.4839	−.4839	1.50	.4332	.1295	.1619	.1457	−.7043	2.00	.4773	.0540	.1620	−.1080	−.2700

(continued)

TABLE D-2. (continued)

z	Area	Ordinate $\phi(z)$	Second derivative $\phi''(z)$	Third derivative $\phi'''(z)$	Fourth derivative $\phi^{iv}(z)$
2.00	.4773	.0540	.1620	−.1080	−.2700
2.01	.4778	.0529	.1609	−.1106	−.2603
2.02	.4783	.0519	.1598	−.1132	−.2506
2.03	.4788	.0508	.1586	−.1157	−.2411
2.04	.4793	.0498	.1575	−.1180	−.2316
2.05	.4798	.0488	.1563	−.1203	−.2222
2.06	.4803	.0478	.1550	−.1225	−.2129
2.07	.4808	.0468	.1538	−.1245	−.2036
2.08	.4812	.0459	.1526	−.1265	−.1945
2.09	.4817	.0449	.1513	−.1284	−.1854
2.10	.4821	.0440	.1500	−.1302	−.1765
2.11	.4826	.0431	.1487	−.1320	−.1676
2.12	.4830	.0422	.1474	−.1336	−.1588
2.13	.4834	.0413	.1460	−.1351	−.1502
2.14	.4838	.0404	.1446	−.1366	−.1416
2.15	.4842	.0396	.1433	−.1380	−.1332
2.16	.4846	.0387	.1419	−.1393	−.1249
2.17	.4850	.0379	.1405	−.1405	−.1167
2.18	.4854	.0371	.1391	−.1416	−.1086
2.19	.4857	.0363	.1377	−.1426	−.1006
2.20	.4861	.0355	.1362	−.1436	−.0927
2.21	.4865	.0347	.1348	−.1445	−.0850
2.22	.4868	.0339	.1333	−.1453	−.0774
2.23	.4871	.0332	.1319	−.1460	−.0700
2.24	.4875	.0325	.1304	−.1467	−.0626
2.25	.4878	.0317	.1289	−.1473	−.0554
2.26	.4881	.0310	.1275	−.1478	−.0484
2.27	.4884	.0303	.1260	−.1483	−.0414
2.28	.4887	.0297	.1245	−.1486	−.0346
2.29	.4890	.0290	.1230	−.1490	−.0279
2.30	.4893	.0283	.1215	−.1492	−.0214
2.31	.4896	.0277	.1200	−.1494	−.0150
2.32	.4898	.0271	.1185	−.1495	−.0088
2.33	.4901	.0264	.1170	−.1496	−.0027
2.34	.4904	.0258	.1155	−.1496	.0033
2.35	.4906	.0252	.1141	−.1495	.0092
2.36	.4909	.0246	.1126	−.1494	.0149
2.37	.4911	.0241	.1111	−.1492	.0204
2.38	.4913	.0235	.1096	−.1490	.0258
2.39	.4916	.0229	.1081	−.1487	.0311
2.40	.4918	.0224	.1066	−.1483	.0362
2.41	.4920	.0219	.1051	−.1480	.0412
2.42	.4922	.0213	.1036	−.1475	.0461
2.43	.4925	.0208	.1022	−.1470	.0508
2.44	.4927	.0203	.1007	−.1465	.0554
2.45	.4929	.0198	.0992	−.1459	.0598
2.46	.4931	.0194	.0978	−.1453	.0641
2.47	.4932	.0189	.0963	−.1446	.0683
2.48	.4934	.0184	.0949	−.1439	.0723
2.49	.4936	.0180	.0935	−.1432	.0762
2.50	.4938	.0175	.0920	−.1424	.0800
2.50	.4938	.0175	.0920	−.1424	.0800
2.51	.4940	.0171	.0906	−.1416	.0836
2.52	.4941	.0167	.0892	−.1408	.0871
2.53	.4943	.0163	.0878	−.1399	.0905
2.54	.4945	.0158	.0864	−.1389	.0937
2.55	.4946	.0154	.0850	−.1380	.0968
2.56	.4948	.0151	.0836	−.1370	.0998
2.57	.4949	.0147	.0823	−.1360	.1027
2.58	.4951	.0143	.0809	−.1350	.1054
2.59	.4952	.0139	.0796	−.1339	.1080
2.60	.4953	.0136	.0782	−.1328	.1105
2.61	.4955	.0132	.0769	−.1317	.1129
2.62	.4956	.0129	.0756	−.1305	.1152
2.63	.4957	.0126	.0743	−.1294	.1173
2.64	.4959	.0122	.0730	−.1282	.1194
2.65	.4960	.0119	.0717	−.1270	.1213
2.66	.4961	.0116	.0705	−.1258	.1231
2.67	.4962	.0113	.0692	−.1245	.1248
2.68	.4963	.0110	.0680	−.1233	.1264
2.69	.4964	.0107	.0668	−.1220	.1279
2.70	.4965	.0104	.0656	−.1207	.1293
2.71	.4966	.0101	.0644	−.1194	.1306
2.72	.4967	.0099	.0632	−.1181	.1317
2.73	.4968	.0096	.0620	−.1168	.1328
2.74	.4969	.0094	.0608	−.1154	.1338
2.75	.4970	.0091	.0597	−.1141	.1347
2.76	.4971	.0089	.0585	−.1127	.1356
2.77	.4972	.0086	.0574	−.1114	.1363
2.78	.4973	.0084	.0563	−.1100	.1369
2.79	.4974	.0081	.0552	−.1087	.1375
2.80	.4974	.0079	.0541	−.1073	.1379
2.81	.4975	.0077	.0531	−.1059	.1383
2.82	.4976	.0075	.0520	−.1045	.1386
2.83	.4977	.0073	.0510	−.1031	.1389
2.84	.4977	.0071	.0500	−.1017	.1390
2.85	.4978	.0069	.0490	−.1003	.1391
2.86	.4979	.0067	.0480	−.0990	.1391
2.87	.4980	.0065	.0470	−.0976	.1391
2.88	.4980	.0063	.0460	−.0962	.1389
2.89	.4981	.0061	.0451	−.0948	.1388
2.90	.4981	.0060	.0441	−.0934	.1386
2.91	.4982	.0058	.0432	−.0920	.1382
2.92	.4983	.0056	.0423	−.0906	.1378
2.93	.4983	.0055	.0414	−.0893	.1374
2.94	.4984	.0053	.0405	−.0879	.1369
2.95	.4984	.0051	.0396	−.0865	.1364
2.96	.4985	.0050	.0388	−.0852	.1358
2.97	.4985	.0049	.0379	−.0838	.1352
2.98	.4986	.0047	.0371	−.0825	.1345
2.99	.4986	.0046	.0363	−.0811	.1337
3.00	.4987	.0044	.0355	−.0798	.1330
3.00	.4987	.0044	.0355	−.0798	.1330
3.01	.4987	.0043	.0347	−.0785	.1321
3.02	.4987	.0042	.0339	−.0771	.1313
3.03	.4988	.0041	.0331	−.0758	.1304
3.04	.4988	.0039	.0324	−.0745	.1294
3.05	.4989	.0038	.0316	−.0732	.1285
3.06	.4989	.0037	.0309	−.0720	.1275
3.07	.4989	.0036	.0302	−.0707	.1264
3.08	.4990	.0035	.0295	−.0694	.1254
3.09	.4990	.0034	.0288	−.0682	.1243
3.10	.4990	.0033	.0281	−.0669	.1231
3.11	.4991	.0032	.0275	−.0657	.1220
3.12	.4991	.0031	.0268	−.0645	.1208
3.13	.4991	.0030	.0262	−.0633	.1196
3.14	.4992	.0029	.0256	−.0621	.1184
3.15	.4992	.0028	.0249	−.0609	.1171
3.16	.4992	.0027	.0243	−.0598	.1159
3.17	.4992	.0026	.0237	−.0586	.1146
3.18	.4993	.0025	.0232	−.0575	.1133
3.19	.4993	.0025	.0226	−.0564	.1120
3.20	.4993	.0024	.0220	−.0552	.1107
3.21	.4993	.0023	.0215	−.0541	.1093
3.22	.4994	.0022	.0210	−.0531	.1080
3.23	.4994	.0022	.0204	−.0520	.1066
3.24	.4994	.0021	.0199	−.0509	.1053
3.25	.4994	.0020	.0194	−.0499	.1039
3.26	.4994	.0020	.0189	−.0488	.1025
3.27	.4995	.0019	.0184	−.0478	.1011
3.28	.4995	.0018	.0180	−.0468	.0997
3.29	.4995	.0018	.0175	−.0458	.0983
3.30	.4995	.0017	.0170	−.0449	.0969
3.31	.4995	.0017	.0166	−.0439	.0955
3.32	.4996	.0016	.0162	−.0429	.0941
3.33	.4996	.0016	.0157	−.0420	.0927
3.34	.4996	.0015	.0153	−.0411	.0913
3.35	.4996	.0015	.0149	−.0402	.0899
3.36	.4996	.0014	.0145	−.0393	.0885
3.37	.4996	.0014	.0141	−.0384	.0871
3.38	.4996	.0013	.0138	−.0376	.0857
3.39	.4997	.0013	.0134	−.0367	.0843
3.40	.4997	.0012	.0130	−.0359	.0829
3.41	.4997	.0012	.0127	−.0350	.0815
3.42	.4997	.0012	.0123	−.0342	.0801
3.43	.4997	.0011	.0120	−.0334	.0788
3.44	.4997	.0011	.0116	−.0327	.0774
3.45	.4997	.0010	.0113	−.0319	.0761
3.46	.4997	.0010	.0110	−.0311	.0747
3.47	.4997	.0010	.0107	−.0304	.0734
3.48	.4998	.0009	.0104	−.0297	.0721
3.49	.4998	.0009	.0101	−.0290	.0707
3.50	.4998	.0009	.0098	−.0283	.0694
3.50	.4998	.0009	.0098	−.0283	.0694
3.51	.4998	.0008	.0095	−.0276	.0681
3.52	.4998	.0008	.0093	−.0269	.0669
3.53	.4998	.0008	.0090	−.0262	.0656
3.54	.4998	.0008	.0087	−.0256	.0643
3.55	.4998	.0007	.0085	−.0249	.0631
3.56	.4998	.0007	.0082	−.0243	.0618
3.57	.4998	.0007	.0080	−.0237	.0606
3.58	.4998	.0007	.0078	−.0231	.0594
3.59	.4998	.0006	.0075	−.0225	.0582
3.60	.4998	.0006	.0073	−.0219	.0570
3.61	.4999	.0006	.0071	−.0214	.0559
3.62	.4999	.0006	.0069	−.0208	.0547
3.63	.4999	.0006	.0067	−.0203	.0536
3.64	.4999	.0005	.0065	−.0198	.0524
3.65	.4999	.0005	.0063	−.0192	.0513
3.66	.4999	.0005	.0061	−.0187	.0502
3.67	.4999	.0005	.0059	−.0182	.0492
3.68	.4999	.0005	.0057	−.0177	.0481
3.69	.4999	.0004	.0056	−.0173	.0470
3.70	.4999	.0004	.0054	−.0168	.0460
3.71	.4999	.0004	.0052	−.0164	.0450
3.72	.4999	.0004	.0051	−.0159	.0440
3.73	.4999	.0004	.0049	−.0155	.0430
3.74	.4999	.0004	.0048	−.0150	.0420
3.75	.4999	.0004	.0046	−.0146	.0410
3.76	.4999	.0003	.0045	−.0142	.0401
3.77	.4999	.0003	.0043	−.0138	.0392
3.78	.4999	.0003	.0042	−.0134	.0382
3.79	.4999	.0003	.0041	−.0131	.0373
3.80	.4999	.0003	.0039	−.0127	.0365
3.81	.4999	.0003	.0038	−.0123	.0356
3.82	.4999	.0003	.0037	−.0120	.0347
3.83	.4999	.0003	.0036	−.0116	.0339
3.84	.4999	.0003	.0034	−.0113	.0331
3.85	.4999	.0002	.0033	−.0110	.0323
3.86	.4999	.0002	.0032	−.0107	.0315
3.87	.5000	.0002	.0031	−.0104	.0307
3.88	.5000	.0002	.0030	−.0100	.0299
3.89	.5000	.0002	.0029	−.0098	.0292
3.90	.5000	.0002	.0028	−.0095	.0284
3.91	.5000	.0002	.0027	−.0092	.0277
3.92	.5000	.0002	.0026	−.0089	.0270
3.93	.5000	.0002	.0026	−.0086	.0263
3.94	.5000	.0002	.0025	−.0084	.0256
3.95	.5000	.0002	.0024	−.0081	.0250
3.96	.5000	.0002	.0023	−.0079	.0243
3.97	.5000	.0002	.0022	−.0076	.0237
3.98	.5000	.0001	.0022	−.0074	.0230
3.99	.5000	.0001	.0021	−.0072	.0224
4.00	.5000	.0001	.0020	−.0070	.0218

(continued)

TABLE D-2. (continued)

x	Area	Ordinate $\phi(x)$	Second derivative* $\phi''(x)$	Third derivative $\phi'''(x)$	Fourth derivative $\phi^{iv}(x)$
4.00	.5000	.0001	.0020	−.0070	.0218
4.01	.5000	.0001	.0019	−.0067	.0212
4.02	.5000	.0001	.0019	−.0065	.0207
4.03	.5000	.0001	.0018	−.0063	.0201
4.04	.5000	.0001	.0018	−.0061	.0195
4.05	.5000	.0001	.0017	−.0059	.0190
4.06	.5000	.0001	.0016	−.0058	.0185
4.07	.5000	.0001	.0016	−.0056	.0180
4.08	.5000	.0001	.0015	−.0054	.0175
4.09	.5000	.0001	.0015	−.0053	.0170
4.10	.5000	.0001	.0014	−.0051	.0165
4.11	.5000	.0001	.0014	−.0049	.0160
4.12	.5000	.0001	.0013	−.0047	.0156
4.13	.5000	.0001	.0013	−.0046	.0151
4.14	.5000	.0001	.0012	−.0044	.0147
4.15	.5000	.0001	.0012	−.0043	.0143
4.16	.5000	.0001	.0011	−.0042	.0138
4.17	.5000	.0001	.0011	−.0040	.0134
4.18	.5000	.0001	.0011	−.0039	.0130
4.19	.5000	.0001	.0010	−.0038	.0127
4.20	.5000	.0001	.0010	−.0036	.0123
4.21	.5000	.0001	.0009	−.0035	.0119
4.22	.5000	.0001	.0009	−.0034	.0116
4.23	.5000	.0001	.0009	−.0033	.0112
4.24	.5000	.0001	.0009	−.0032	.0109
4.25	.5000	.0001	.0008	−.0031	.0105
4.26	.5000	.0001	.0008	−.0030	.0102
4.27	.5000	.0000	.0008	−.0029	.0099
4.28	.5000	.0000	.0007	−.0028	.0096
4.29	.5000	.0000	.0007	−.0027	.0093
4.30	.5000	.0000	.0007	−.0026	.0090
4.31	.5000	.0000	.0007	−.0025	.0087
4.32	.5000	.0000	.0006	−.0024	.0085
4.33	.5000	.0000	.0006	−.0023	.0082
4.34	.5000	.0000	.0006	−.0022	.0079
4.35	.5000	.0000	.0006	−.0022	.0077
4.36	.5000	.0000	.0005	−.0021	.0074
4.37	.5000	.0000	.0005	−.0020	.0072
4.38	.5000	.0000	.0005	−.0019	.0070
4.39	.5000	.0000	.0005	−.0019	.0067
4.40	.5000	.0000	.0005	−.0018	.0065
4.41	.5000	.0000	.0004	−.0017	.0063
4.42	.5000	.0000	.0004	−.0017	.0061
4.43	.5000	.0000	.0004	−.0016	.0059
4.44	.5000	.0000	.0004	−.0016	.0057
4.45	.5000	.0000	.0004	−.0015	.0055
4.46	.5000	.0000	.0004	−.0014	.0053
4.47	.5000	.0000	.0004	−.0014	.0052
4.48	.5000	.0000	.0003	−.0013	.0050
4.49	.5000	.0000	.0003	−.0013	.0048
4.50	.5000	.0000	.0003	−.0012	.0047
4.50	.5000	.0000	.0003	−.0012	.0047
4.51	.5000	.0000	.0003	−.0012	.0045
4.52	.5000	.0000	.0003	−.0012	.0044
4.53	.5000	.0000	.0003	−.0011	.0042
4.54	.5000	.0000	.0003	−.0011	.0041
4.55	.5000	.0000	.0003	−.0010	.0039
4.56	.5000	.0000	.0002	−.0010	.0038
4.57	.5000	.0000	.0002	−.0010	.0037
4.58	.5000	.0000	.0002	−.0009	.0035
4.59	.5000	.0000	.0002	−.0009	.0034
4.60	.5000	.0000	.0002	−.0009	.0033
4.61	.5000	.0000	.0002	−.0008	.0032
4.62	.5000	.0000	.0002	−.0008	.0031
4.63	.5000	.0000	.0002	−.0008	.0030
4.64	.5000	.0000	.0002	−.0007	.0028
4.65	.5000	.0000	.0002	−.0007	.0027
4.66	.5000	.0000	.0002	−.0007	.0026
4.67	.5000	.0000	.0002	−.0006	.0026
4.68	.5000	.0000	.0002	−.0006	.0025
4.69	.5000	.0000	.0001	−.0006	.0024
4.70	.5000	.0000	.0001	−.0006	.0023
4.71	.5000	.0000	.0001	−.0006	.0022
4.72	.5000	.0000	.0001	−.0005	.0021
4.73	.5000	.0000	.0001	−.0005	.0020
4.74	.5000	.0000	.0001	−.0005	.0020
4.75	.5000	.0000	.0001	−.0005	.0019
4.76	.5000	.0000	.0001	−.0005	.0018
4.77	.5000	.0000	.0001	−.0004	.0018
4.78	.5000	.0000	.0001	−.0004	.0017
4.79	.5000	.0000	.0001	−.0004	.0016
4.80	.5000	.0000	.0001	−.0004	.0016
4.81	.5000	.0000	.0001	−.0004	.0015
4.82	.5000	.0000	.0001	−.0004	.0015
4.83	.5000	.0000	.0001	−.0003	.0014
4.84	.5000	.0000	.0001	−.0003	.0013
4.85	.5000	.0000	.0001	−.0003	.0013
4.86	.5000	.0000	.0001	−.0003	.0012
4.87	.5000	.0000	.0001	−.0003	.0012
4.88	.5000	.0000	.0001	−.0003	.0012
4.89	.5000	.0000	.0001	−.0003	.0011
4.90	.5000	.0000	.0001	−.0003	.0011
4.91	.5000	.0000	.0001	−.0002	.0010
4.92	.5000	.0000	.0001	−.0002	.0010
4.93	.5000	.0000	.0001	−.0002	.0009
4.94	.5000	.0000	.0001	−.0002	.0009
4.95	.5000	.0000	.0000	−.0002	.0008
4.96	.5000	.0000	.0000	−.0002	.0008
4.97	.5000	.0000	.0000	−.0002	.0008
4.98	.5000	.0000	.0000	−.0002	.0008
4.99	.5000	.0000	.0000	−.0002	.0007

*

$$\phi(X) = \frac{1}{\sqrt{2\pi}} e^{-\frac{X^2}{2}}$$

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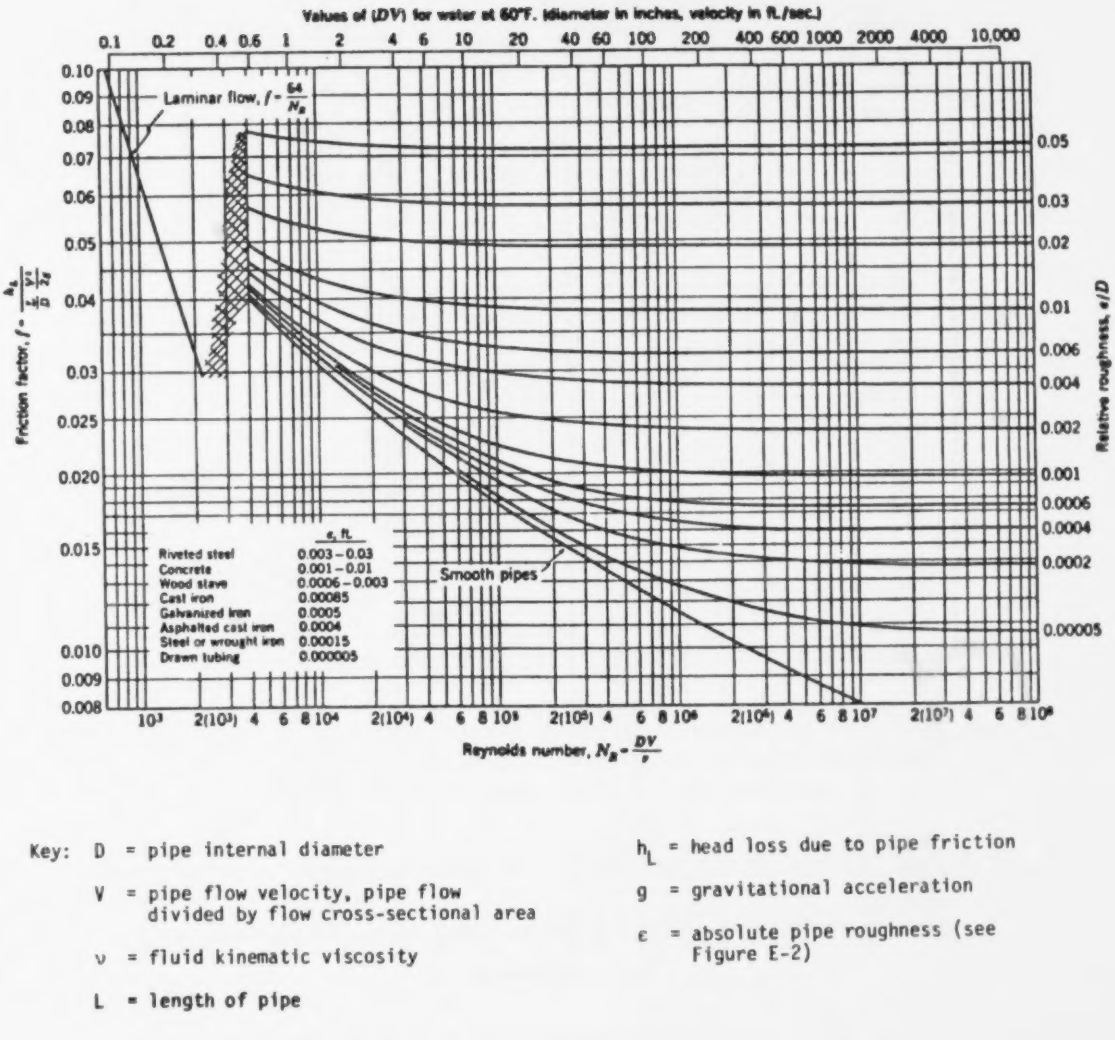
APPENDIX E

PIPE FLOW DATA



Key: D = pipe internal diameter

V = pipe flow velocity, pipe flow divided by flow cross-sectional area

ν = fluid kinematic viscosity

L = length of pipe

h_L = head loss due to pipe friction

g = gravitational acceleration

ε = absolute pipe roughness (see Figure E-2)

Figure E-1. Moody diagram for estimating the friction factor for pipes (after Linsley and Franzini, 1964).

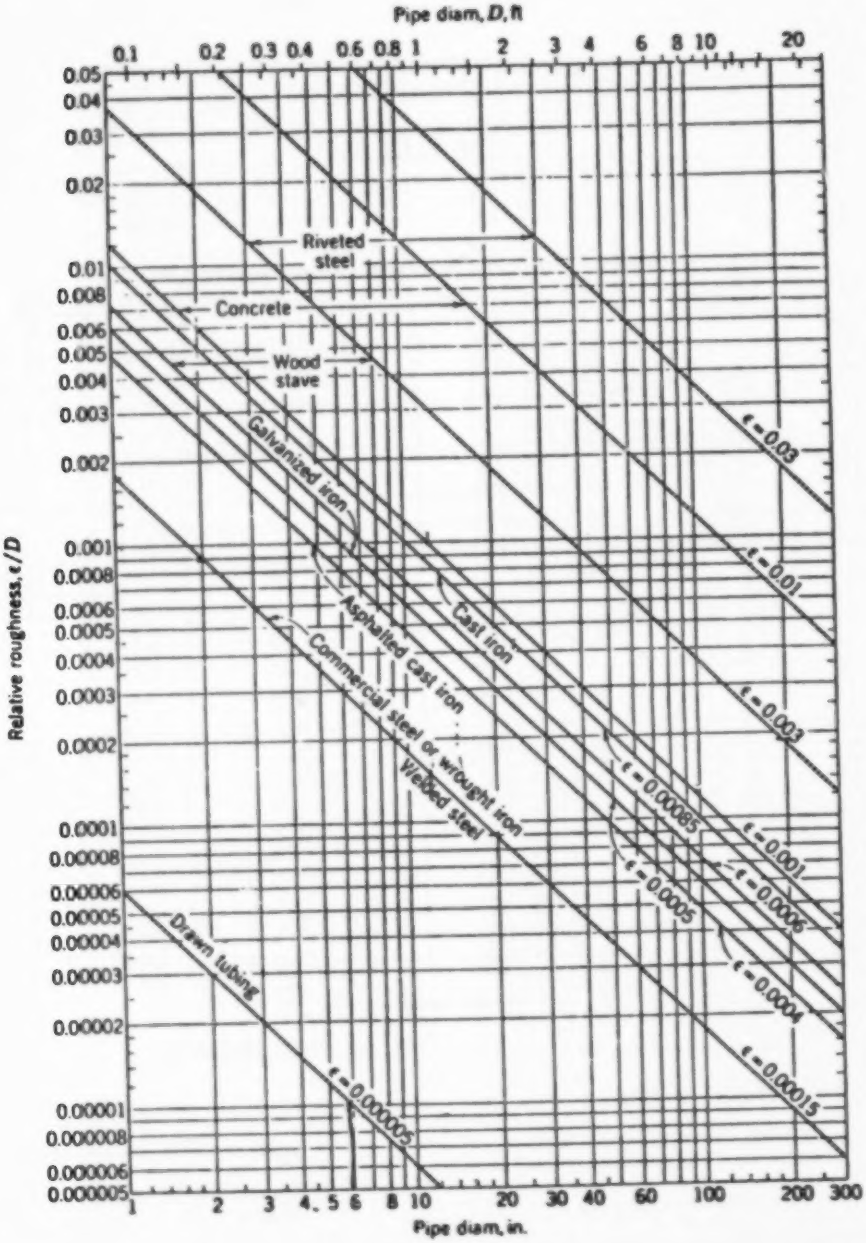


Figure E-2. Relative roughness for different types of pipes (after Moody, 1944).

TABLE E-1. PHYSICAL PROPERTIES OF LIQUID WATER

Temp, °F	Specific weight γ, pcf	Density ρ, slugs/ft³	* Viscosity $\mu \times 10^5$, lb-sec/ft²	* Kinematic viscosity $\nu \times 10^5$, ft²/sec	* Surface tension $\sigma \times 10^2$, lb/ft	Vapor pressure head p_v/γ, ft	* Bulk modulus of elasticity $K \times 10^{-3}$, psi
32	62.42	1.940	3.746	1.931	0.518	0.20	293
40	62.43	1.940	3.229	1.664	0.514	0.28	294
50	62.41	1.940	2.735	1.410	0.509	0.41	305
60	62.37	1.938	2.359	1.217	0.504	0.59	311
70	62.30	1.936	2.050	1.059	0.500	0.84	320
80	62.22	1.934	1.799	0.930	0.492	1.17	322
90	62.11	1.931	1.595	0.826	0.486	1.61	323
100	62.00	1.927	1.424	0.739	0.480	2.19	327
110	61.86	1.923	1.284	0.667	0.473	2.95	331
120	61.71	1.918	1.168	0.609	0.465	3.91	333
130	61.55	1.913	1.069	0.558	0.460	5.13	334
140	61.38	1.908	0.981	0.514	0.454	6.67	330
150	61.20	1.902	0.905	0.476	0.447	8.58	328
160	61.00	1.896	0.838	0.442	0.441	10.95	326
170	60.80	1.890	0.780	0.413	0.433	13.83	322
180	60.58	1.883	0.726	0.385	0.426	17.33	318
190	60.36	1.876	0.678	0.362	0.419	21.55	313
200	60.12	1.868	0.637	0.341	0.412	26.59	308
212	59.83	1.860	0.593	0.319	0.404	33.90	300

Source: From Fluid Mechanics by Daugherty and Franzini. Copyright © 1965 by McGraw-Hill, used with permission of McGraw-Hill Book Company.

*Note values in the columns are interpreted in the following way:

For Temp. = 40°F $\mu = 3.229 \times 10^{-5}$, $\nu = 1.664 \times 10^{-5}$, $\sigma = .514 \times 10^{-2}$, and $K = 294 \times 10^{3}$.

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APPENDIX F

EXAMPLE CASE

INTRODUCTION

In this section the methodology is applied to a hypothetical geothermal power plant to illustrate the sequence of the procedure. The power plant is a 50 MWe single cycle flash type. The plant is located in an agricultural area with sandy soils. Ten production wells and five injection wells serve the plant. Preinjection treatment ponds and a temporary storage pond are located at the site.

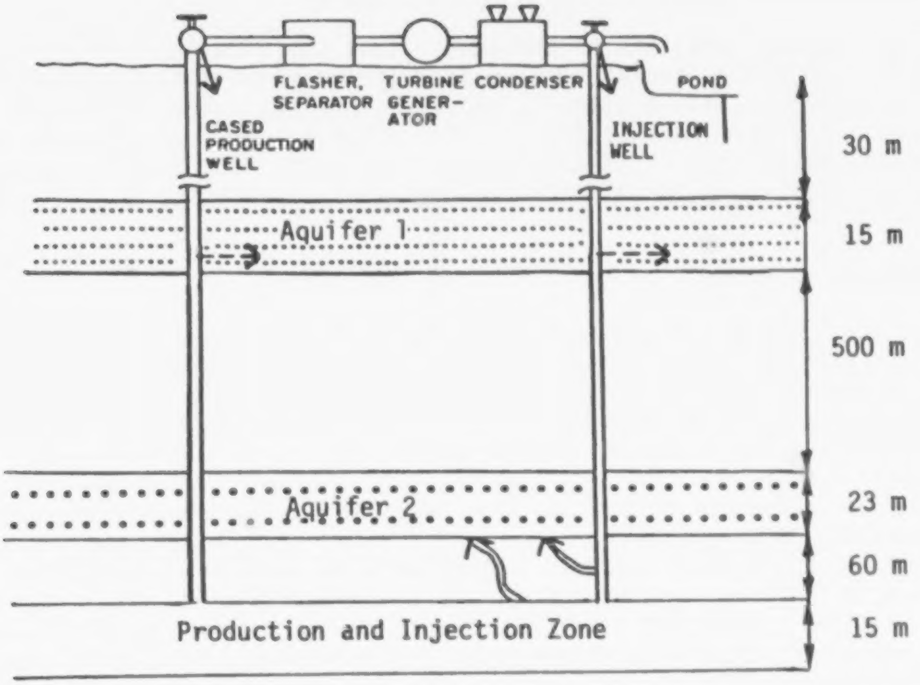
Two aquifers underlying the site are used in the nearby area. Aquifer 1 is a shallow aquifer used as a drinking water supply for the surrounding population. Aquifer 2 is a deeper aquifer used as an irrigation supply. A typical cross-section at the plant site is shown in Figure F-1. The production zone is located 60 meters below Aquifer 2. The spent geothermal fluid is injected back into the production zone after passing through ponds to precipitate silica and to remove suspended solids.

SITE CHARACTERISTICS

Power plant capacity	50 MWe
Production well flow rate	1,000 gpm
Injection well flow rate	2,000 gpm
Total fluid flow rate	10,000 gpm

Geothermal fluid characteristics:

Total dissolved solids	4,400 mg/ℓ	Alkalinity	390 mg/ℓ (as $CaCO_3$)
Arsenic	0.15 mg/ℓ	Barium	2.9 mg/ℓ
Boron	4.3 mg/ℓ	Cadmium	0.02 mg/ℓ
Chloride	2,760 mg/ℓ	Iron	1.2 mg/ℓ
Manganese	0.28 mg/ℓ	Mercury	0.006 mg/ℓ


FLASHER, SEPARATOR
TURBINE GENERATOR
CONDENSER
POND
CASED PRODUCTION WELL
INJECTION WELL
30 m
Aquifer 1
15 m
500 m
Aquifer 2
23 m
60 m
Production and Injection Zone
15 m

NOTE: Diagram not to scale.

Key:

Release Type

→ Group 1

--> Group 2

⇒ Group 3

Figure F-1. Typical cross-section at power plant site.

Selenium	0.5 mg/ℓ	Sodium	1,619 mg/ℓ
Temperature at well bottom		180°C	

PROBLEM STATEMENT

A preliminary analysis of the power plant and site identified three potential problems. They are a leak from the temporary storage pond, a leak through the casing into Aquifer 1, and a casing leak in the injection well which could migrate into Aquifer 2. The following sections describe how the methodology would be used to estimate the concentrations from these hypothetical releases and to evaluate the potential significance.

ENVIRONMENTAL CONCERNS

The two aquifers of concern were identified from well records and test drilling at the site (see Figure F-1). Interconnections between Aquifers 1 and 2 are considered minimal because of the very low permeability of the shale formation between them and the absence of known faults or fractures in the shale.

Aquifer uses were determined from water rights permits and a survey of farmers in the area. Aquifer 1 is used as a drinking water supply for about 150 people and for stock watering. Aquifer 2 is used as an irrigation supply for about 50 farms. A comparison of the concentrations in the geothermal fluid with EPA primary and secondary drinking water standards for Aquifer 1 and agricultural use limits for Aquifer 2 identified several constituents of concern (Table F-1).

RELEASE POTENTIAL

Potential release points are identified by reviewing the power plant schematic and comparing it to Figure 8 Diagram to Locate Potential Releases. The geothermal fluid concentrations and power plant conditions are then compared to the threshold values to identify cases where high pressures, temperatures, hydrogen sulfide or TDS concentrations occur. In this example case pressures slightly above 100 psia exist in the power plant and injection well. None of the other threshold values are exceeded. Potential release sites are casing leaks in an injection well, pipe breaks at elbows, and leaks from the unlined storage pond. Three release types are further described to illustrate the other sections of the methodology: a pond leak, a casing leak from the injection well into Aquifer 1, and a casing leak in the injection well which could migrate to Aquifer 2.

Release volumes are estimated for each of these cases based on well and plant flows and Table 20. A slow leak from the pond might have a flow rate of 450 gpd. Casing leaks in the injection well would have a maximum flow rate of 2,000 gpm.

TABLE F-1. CHEMICAL PARAMETERS OF CONCERN

Constituent	Geothermal fluid concentrations, mg/ℓ	Drinking water standards* units are mg/ℓ	Irrigation limits units are mg/ℓ**
Arsenic	0.15	0.05	0.1
Barium	2.9	1.0	-[†]
Boron	4.3	-	0.75
Cadmium	<0.02	0.01	1
Chloride	2,760	250	-
Iron	1.2	0.3	-
Lead	0.4	0.05	30
Manganese	0.28	0.05	0.2 for acidophilic plants
Mercury	0.006	0.002	-
Selenium	0.5	0.01	-
Sodium	1,619	-	high SAR
Total dissolved solids	4,422	500	1,500

*U.S. EPA, 1976a and 1977.

**U.S. EPA, 1976b.

[†] Dash indicates no criteria.

CHEMISTRY OF RELEASED FLUID

The temperature of the fluid at the well bottom is 180°C and 104°C at the injection wellhead. The pressure drops from 160 psia at the well bottom to 103 psia at the injection well. The geothermal fluid moves up the well and flashes at the production wellhead. The steam is routed to a turbine and condenser and then is mixed with the unflashed fluid from the flash vessel. The combined fluid then goes to the injection treatment pond and injection well. Leaks in the part of the plant where the fluid is separated into two phases are not likely so corrections to the fluid concentrations do not need to be made.

GROUND WATER CONTAMINATION

The first step is to determine the appropriate solution method for the three release cases using Table 24, Summary of Solution Methods. The slow leak from the storage pond is a Group 1 continuous release. The appropriate solution method is GEOHY-GEOQAL Analytical Solution and the mass-balance approach. The leak from the injection well casing into Aquifer 1 is a Group 2 slug release; the well was shut-in one hour after discovery of the leak. The appropriate solution method is Advection-Dispersion Case A. The leak from the injection well which migrates into Aquifer 2 is a Group 3 slug release since the well was shut-in after 12 hours. The appropriate solution method is the Bernoulli-Darcy method and Advection-Dispersion Case A. The following sections describe the equations to be used and how they apply to these cases. Numerical values have not been substituted into the equations since the emphasis is on the procedure.

GROUP 1 SURFACE RELEASE

Problem Statement

Estimate the time required for the concentration of pollutant X at a depth of 30 meters to be fifty and ninety percent of the initial concentration in the geothermal fluid. The soils are sandy with a seepage velocity of 0.15 m/day. A tracer study in the field gave a value of 0.011 m^2/day for vertical dispersion.

Solution Method

The release is a Group 1 continuous release. Since the problem is to determine when the concentration has reached a given value the procedure for breakthrough times can be used. The equation to be used to calculate the fifty percent value is Eq. (10):

$$t_{1/2} = \frac{z\gamma}{v_s} = \frac{z}{v_s}\left(1 + \frac{k}{\varepsilon}\right) , \qquad (10)$$

where all terms are as defined in Section 4.

Data needed are depth of interest, seepage velocity, void volume in the soil, and the adsorption equilibrium constant. The first two values were determined in the field and are given in the problem statement. The void volume is estimated from the porosity. The porosity is .25 as estimated from cores. The adsorption constant should be set equal to 0 initially and then may be set equal to the appropriate value, e.g., 400 for mercury. The data are then substituted into Eq. (10).

The time to reach ninety percent of the initial concentration at 30 m is estimated using the simplified form of Eq. (13):

$$R = \gamma m \left[1 \pm \sqrt{1 - \frac{1}{m^2}} \right]$$

where $m = \left(1 + St'^2 \right)$ and other terms are as defined in Section 4

and

$$t_{90} = \frac{R_z}{V_s} .$$

The resulting concentration in Aquifer 1 is estimated by the mass balance approach using Eq. (14):

$$c = \frac{Q_p c_p + Q_A c_A}{Q_p + Q_A} \tag{14}$$

This approach assumes complete mixing with that portion of the aquifer directly under the pollutant source. Data needed include the area and width of the pond, the velocity of the pollutant, the thickness and velocity of the aquifer, the initial concentration of pollutant in the aquifer and the concentration at the aquifer interface. The concentration at the aquifer interface can be considered equal to the initial pollutant concentration for a worst case or estimated using Eq. (8):

$$\frac{c(z,t)}{c_o} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{R - \gamma}{\sqrt{4R\gamma S}} \right) \right] \tag{8}$$

The resulting concentration in Aquifer 1 is then compared to the drinking water standards.

GROUP 2 RELEASE

Problem Statement

Estimate maximum concentration in Aquifer 1 from a casing leak in the injection well at a distance of 30 m. The flow rate was 760 ℓpm for one hour which gives a total release volume of 45,600 ℓ. The seepage velocity in Aquifer 1 is 0.03 m/day. Dispersion tests in the field gave a lateral dispersion rate of 0.46 m^2/day.

Solution Method

The time to reach the maximum concentration at the specified distance is estimated first, using Eq. (18):

$$t_{max} = \frac{\left(\sqrt{1 + \left(\frac{V_s r'}{nD_x}\right)^2} - 1\right) n\, D_x}{V_s^{\,2}} \qquad (18)$$

Data needed are the seepage velocity, the lateral dispersion and the desired distance. The maximum time is then used as data input to estimate the maximum concentration at the desired distance using Eq. (17):

$$c(x,y,t) = \frac{1}{R_d} \; \frac{m'}{4\pi p t (D_x D_y)^{1/2}} \; \exp\left[- \frac{(x - V_s t)^2}{4D_x t} - \frac{y^2}{4D_y t} - \lambda t \right] \qquad (17)$$

Additional data needed include total mass of pollutant injected into the aquifer, effective porosity, adsorption constant, and void volume. The mass of pollutant is estimated as the volume of released fluid times the pollutant concentration. The mass is then expressed as mass per meter of aquifer thickness. The conservative case would be estimated first by assuming no adsorption so $R_d = 1$.

The concentrations for the conservative case would be compared to the drinking water standards. For the constituents which exceed the standards then the concentrations with attenuation are estimated. For these cases the retardation factor, R_d, would be computed using the appropriate adsorption constant, k.

GROUP 3 RELEASE

Problem Statement

Estimate the flow and concentration in Aquifer 2 from a leak in the casing of an injection well. The injection well had a flow rate of 7,600 ℓpm. The well flowed for 12 hours before it was shut-in. The location of the leak was 250 meters below the surface. The well casing is 0.3 meters in diameter and is made of carbon steel.

Solution Method

The flow into Aquifer 2 can be estimated using the Bernoulli-Darcy approach. The pressure at the point of the leak is estimated using Eq. (19):

$$\frac{P_2}{\gamma} = \frac{P_1}{\gamma} + L + f\,\frac{L}{D}\,\frac{V_1^{\,2}}{2_g} \tag{19}$$

Data needed are the wellhead pressure, the depth to the leak, the well diameter, the friction factor of the casing, and the velocity in the well. The friction factor is estimated from the Moody diagram (Figure E-1 in Appendix E based on the relative roughness and Reynolds number. The roughness is estimated from Figure E-2 in Appendix E. The Reynolds number is estimated from Eq. (20):

$$N_R = \frac{DV}{\nu} \tag{20}$$

The next step is to estimate the pressure at the casing leak using Eq. (19).

The flow into Aquifer 2 is estimated using a modified form of Darcy's Law. The shale between the injection zone and Aquifer 2 is known to be fractured. The fracture zone is considered to be a circular zone 0.6 m in diameter with a permeability of 7.6 m/day. Aquifer 2 is confined with a hydrostatic head of 60 m. The flow into Aquifer 2 is estimated using Eq. (21):

$$Q_3 = KA\left(\frac{\frac{P_2}{\gamma} - \frac{P_3}{\gamma}}{(Z_3 - Z_2)}\right) \tag{21}$$

Data needed include the permeability, approximate length, and cross-sectional area of the fracture zone, the pressure in Aquifer 2, the head in the aquifer, and the specific weight of the geothermal fluid.

The resulting concentration in the aquifer can be estimated in the same manner as the Group 2 release using Eq. (17) and (18). These concentrations would be compared to the agricultural use limits (Table 11).

APPENDIX G

GLOSSARY OF SELECTED TERMS

Seepage velocity - a microscopic property, actual velocity of fluid flow through interstices of the soil.

Darcy velocity - a macroscopic property, the velocity of fluid in the ground water system as defined by Darcy's Law, $V = -K\frac{dh}{dT}$, where K = hydraulic conductivity, $\frac{dh}{dT}$ = hydraulic gradient.

Field capacity - water content of a soil profile which has been thoroughly wetted and allowed to drain until the rate of drainage is negligible.

Adsorption - the attachment of pollutants to soil material by various mechanisms including for example, cation exchange.

Advection - the movement of solutes by flowing ground water at a rate equal to the average velocity of the water.

Dispersion - the spreading of solutes as they are transported by advection. Dispersion is caused by microscopic differences in pore velocities and by the mixing of fluid in individual pore channels.

Longitudinal dispersion - the spreading of solutes in the direction of flow.

Transverse dispersion - the spreading of solutes perpendicular to the direction of flow.

APPENDIX H

U.S.-METRIC CONVERSION TABLE

U.S. customary	U.S. equivalent	Metric equivalent
	Length	
inch (in)	0.083 ft	25.4 millimeters (mm)
foot (ft)	0.33 yd, 12 in	0.3048 meters (m)
yard (yd)	3 ft, 36 in	0.9144 m
mile (mi)	5,280 ft, 1,760 yd	1.609 kilometers (km)
	Area	
square foot (sq ft)	144 sq in	0.0929 sq m
square yard (sq yd)	1,294 sq in, 9 sq ft	0.836 sq m
acre	43,560 sq ft, 4,840 sq yd	4,047 sq m, 0.404 hectare (ha)
square mile (sq mi)	640 acres	2.59 sq km
	Volume	
gallon	4 quarts	3.785 liters (ℓ)
cubic yard (cu yd)	27 cu ft	7.645 cubic meter (cu m)
cubic mile (cu mi)		4.1655 cu km
	Flow Rate	
gallons per minute (gpm)		3.785 liters per minute (ℓpm), 6.309×10^{-5} cu m/sec
18.2 gpd/sq ft (for water at 60°F)	Darcy	9.66×10^{-4} cm/sec (for water at 20°C)
pounds per hour		1.260×10^{-4} kg/sec
cu ft per sec (cfs)		28.32 ℓps, 0.02831 cu m/sec

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16. ABSTRACT

This report provides analytical methods and graphical techniques to predict potential ground water contamination from geothermal energy development. Overflows and leaks from ponds, pipe leaks, well blowouts, leaks from well casing, and migration from injection zones can be handled by the methodology. General characteristics of geothermal systems and fluids and probable modes of release are included in the report to provide typical data.

The major steps of the procedure are to determine environmental concerns and release potential, to identify potential ground water contamination, and to evaluate significance of contamination. Analytical methods, data requirements. typical data and coefficient values are included.

The methodology may be used as a regulatory tool for predicting impacts or for testing control technologies. Geothermal developers can use the methodology to predict adverse impacts at development sites and select control methods for the conditions or locations where required.

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Geothermal prospecting	water pollution	13B
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